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16. ABSTRACT

The report documents presentations at the fifth EPA-sponsored symposium on the environmental aspects of fuel conversion technology, in St. Louis, MO, 9/16-19/80. The symposium served as a colloquium on environmental information related to coal gasification, indirect liquefaction, and direct liquefaction. The program included sessions on program approach, environmental assessment, and environmental control, including the development of EPA's pollution control guidance documents. Process developers and users, research scientists, and State and Federal officials participated in the symposium.

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PREFACE

These proceedings for the symposium on "Environmental Aspects of Fuel Conversion Technology" constitute the final report submitted to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency (IERL-EPA), Research Triangle Park, N.C. The symposium was conducted at the Chase-Park Plaza Hotel in St. Louis, Missouri, September 16-19, 1980.

This symposium served as a colloquium on environmental information related to coal gasification and liquefaction. The program included sessions on program approach, environmental assessment for both direct and indirect liquefaction and for gasification, and environmental control—including the development of the EPA's pollution control guidance documents. Process developers and users, research scientists and State and Federal officials participated in this symposium, the fifth to be conducted on this subject by IERL-RTP since 1974.

Dr. N. Dean Smith, Gasification and Indirect Liquefaction Branch, EPA-IERL, Research Triangle Park, N.C., was the Project Officer and the Technical Chairman. Mr. William J. Rhodes, Synfuel Technical Coordinator for EPA-IERL-RTP, was General Chairman.

Mr. Franklin A. Ayer, Manager, Technology and Resource Management Department, and Mr. N. Stuart Jones, Analyst, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, N.C., were symposium coordinators and compilers of the proceedings.

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OPENING SESSION

KEYNOTE ADDRESS

by

KURT W. RIEGEL, Ph.D.

Associate Deputy Assistant Administrator

Office of Environmental Engineering and Technology

U. S. Environmental Protection Agency

Good morning. On behalf of the Environmental Protection Agency, I welcome you to our Fifth Symposium on the Environmental Aspects of Fuel Conversion Technology. Since our Fourth Symposium in Hollywood last year, much has happened, but two things in particular now inspire our research efforts: First, the price of imported oil has continued to skyrocket. For example, from June 1979 to June 1980, the price increased from an average of $18.90 to $31.60 per barrel--not counting spot market surcharges. Second, the President has signed into law the Synthetic Fuels Corporation Bill authorizing up to $20 billion to encourage the growth of a synthetic fuels industry in the United States. These two stimuli--among others--appear to me to insure that the synthetic fuels industry will be real--established and thriving--well before the end of the century.

As environmental protection scientists and technologists, we have had a unique opportunity to study the various synthetic fuels processes in embryo and to lay the basis for sound environmental development of the industry. This is in sharp contrast to the situation we have faced with countless other industries, where after-the-fact environmental regulations have been resented and challenged, either legally or politically. After the oil embargo in late 1973, we prepared to respond to the environmental challenge of a rapidly growing synthetic fuels industry that, according to the Project Independence Blueprint, loomed large on the horizon. That shadow has been looming and receding through many cycles in the past six years. As you all know, we have suffered on-again, off-again funding in response, but we have somehow managed to sustain a core effort through all of these gyrations.

Perhaps it is just as well that our day of reckoning has been delayed. We have learned a great deal more about the processes and pollutants and have seen the evolution of more comprehensive Federal environmental laws. New acronyms and areas of concern have appeared since 1974: TOSCA, RCRA, priority pollutants, hazardous solid wastes, etc. Each new law has broadened our perception of our task to characterize the waste streams from synthetic fuels technologies, to find appropriate environmental control technologies, and to formulate a comprehensive data base for the use of EPA's Program Offices, as they put together effective, economically feasible regulations.

Another important gain during this period has been the refinement of the communications channels between DOE and EPA through interagency programs. In response to President Carter's directive of May 23, 1977, that EPA and DOE jointly develop procedures for establishing environmental standards for all new energy technologies, a Memorandum of Understanding between DOE and EPA has been executed. This formalizes the many fruitful contacts that have been developed at the various working levels between these organizations.

Further, within the Agency the Alternate Fuels Group and the Priority Energy Project Group have been established by Doug Costle to consider the environmental policy issues involved in implementing the National Energy Program and to coordinate EPA activities for appropriate responses to these issues.

This morning I would like to briefly review the course of our odyssey over the past six years and then discuss with you what I believe will be done in the near future.

The EPA's Synthetic Fuels Program was initiated in the early 1970's but received a boost in 1974, following OPEC's import embargo and in parallel with the preparation of President Nixon's Project Independence Blueprint. The schedules that were originally laid out for our assessments were based upon the apparent national schedules for synfuel commercialization in the 1976 time period. However, private investors balked at putting capital into plants to produce liquids or high BTU gas which could not compete in price with natural fossil fuels then or in the foreseeable future. As ERDA's (now DOE's) Synthetic Fuels Commercialization Program had failed to gain Congressional approval, there was no basis for expecting any major Federal support of commercialization activity, and the EPA therefore targeted the completion of the synfuels program for the 1984-86 time period, which would allow time for application of our results to plant designs.

So, the EPA's program started rolling in needed data, ERDA/DOE's program started rolling out development concepts, and--what nobody had anticipated--OPEC continued rolling up crude oil prices at an ever-increasing rate. Oil which had cost us $3.50 per barrel in mid-1973 was over $12.00 per barrel in mid-1977. It rose to over $18.00 per barrel in mid-1979 and was almost $32.00 per barrel in June of this year. This escalation has had two major effects: the Federal government, seeing the continually climbing monthly cost of supporting our crude oil demands through imports and recognizing the damage being done to both our domestic and foreign economic positions, made a decision not only to support synfuels commercialization, but also to establish a means of speeding permit and regulation compliance by developers. The organization proposed to handle these tasks was the Synfuels Corporation.

Meanwhile, entirely separate from these legislative activities, a number of commercial interests noted that the economics of operating large-scale, coal-to-gasoline or methanol plants became favorable and indicated a reasonable return on investment at retail unit prices of $1.00 to $1.25 for gasoline at the pump. As a consequence, a series of completely independent, privately financed synfuel projects were announced, ranging over the major coal seams of the country, and with schedules indicating operation in the 1984-88 time period.

I said earlier that our programs were targeted for completion in about the same time period. It follows that there is no way that a plant that starts operating at the time that our program is completed could possibly utilize our input or data, and the controls on that plant's waste streams would probably be based upon best engineering judgement. Furthermore, neither our regional permit offices nor the local state and county offices would have had a sound basis for evaluating the permit applications submitted for that plant. Again, best engineering judgement would have been applied in the evaluation process. It was, therefore, very clear that the EPA needed both a means of dealing with accelerated projects and a basis for rationally and objectively evaluating forthcoming plant permit applications.

Both of these needs represented areas in which the "traditional" EPA approaches could not be applied. Simply stated, our data acquisition and analysis program was not complete, and, therefore, we were not in a position to write firm "traditional" regulations covering waste discharges to all media. Furthermore, the EMB charter contained the option of selecting and recommending certain environmental and other regulations for executive branch set-aside, and we really didn't have sufficient data to effectively argue all of the set-asides.

To address both of these needs, the EPA administrator created operational arms for the use of the existing, formerly advisory, EPA Energy Policy Committee. The first of these, the Priority Energy Project Group focused on the development of a working relationship with the EMB and had four major objectives:

First, the Group would draft EPA procedures and guidance for developing regulations in support of the EMB and for performing as an accelerator of designated priority energy projects. Second, it would be responsible for the development of a system for tracking permit processing information, from submittal through approval or rejection. Third, it would provide information on EPA permitting procedures, thereby influencing the development of EMB procedures and assisting both the applicants and the permitting agencies in understanding the total process. Finally, the Group would serve as EPA's principal liaison with the EMB.

The second recently created working arm of the EPC is the Alternate Fuels Group (or AFG), which has a longer listing of responsibilities involving the Agency's regulatory, permitting, and research strategy for synthetic and other alternate fuels. This group addresses all synfuels, and its overall goal is to deal with our assessment data gap, both as a current problem and in terms of eliminating it as a problem in the near future. The Group's work plan logically divides into three areas: First, defining where we are and what the Agency position on the major issues is right now. This will be accomplished through publication of our Agency environmental summary paper, which we plan to update periodically.

Second, the group will prepare Agency guidance, in advance of our traditional regulations, on the best available controls for application to synfuel plant waste streams. This will lead to direct input to the EPA regulatory offices in support of their later development of standards for the synfuels industry.

And third, the group will prepare an R, D&D plan for the overall synthetic fuel program under the Office of Research and Development. This plan, to cover approximately a 5-year period, will address the options, priorities, and means of filling the data gaps and supporting the expeditious development of regulations.

I'd like to drop back to the second element of the AFG's work plan. Since this area--that is, the early guidance--is in current demand, I think it's worthwhile describing where we are in more detail.

To assist in accomplishing its work assignments, the AFG has defined four Working Groups, covering the major synfuel product areas. The areas are Gasification/Indirect Liquefaction, Direct Liquefaction, Oil Shale, and Biomass. Each of these Working Groups is drafting guidance in its particular area; all are working to virtually the same outline and format requirements; and all are treating the shared or common technology areas in the same fashion. For example, the impact on plant costs and operating economics is being handled in basically the same way by all groups.

The product guidance will be Agency guidance and will cover all media plus toxic substances and radiation. It will be approved for release by all of the responsible EPA Program Offices as Pollution Control Guidance Documents, or PCGD's. There are three principal target of this guidance. First are the permit reviewers, both in the EPA regional offices and in the comparable State government agencies. Second are the process developers or permit applicants who want to construct synfuel plants: And third are the regulatory offices, which will utilize the data base as an input for standards preparation.

The technical approach being taken by all Working Groups is, in brief, to collect and analyze all available environmental and process data in order to synthesize Agency positions on the best available control approaches achievable at a reasonable cost. The PCGD's will present the available process characterization and control data and the analyses utilized in formulating guidance as an appendix. The presentation of the data base will enable the regulatory offices to evaluate issues (such as how to handle discharges of potentially dangerous but presently unregulated pollutants) and aid them in deciding how and when to develop standards. It should also serve to convince system developers that all reasonable control options have been considered and to show interested environmental groups that the permitting offices have the tools needed to protect the environment through the recommendation of specific controls. Additionally, through the implementation of a multicycle review process, the comments and criticism of key industry personnel are being obtained as the PCGD's evolve through several draft stages. This direct participation will, we hope, further serve to convince industry of the thoroughness of our approach and that it is in their best interest to use the PCGD recommendations and guidance in their designs and permit applications.

I don't want to give the impression that we are rapidly constructing some boxes and at the same time trying to convince a number of interested groups that they'll be happy in them--not so at all.

The PCGD's will provide detailed guidance on the best control practice (a single control) for each stream, plus provide information on other approaches relative to cost, energy requirements and residuals. In additional, for those streams considered to be significant environmental problems or whose control can have major cost impacts, one or more options for achieving greater pollutant content reductions or lesser cost will be presented.
Options which combine controls between process segments or utilize waste materials (both gases and liquids) as plant fuel will be included. And for everyone's benefit, a detailed "How-to-use-the-PCGD" section, with examples, will be provided.

So, as you can see, the boxes are designed to be comfortable for everyone and to cover everyone's needs as best we can at this point in time. Naturally, we'll update the PCGD's as additional data are developed and analyzed in our research program, until firm standards and regulations are promulgated.

As you all know, the provision of the Energy Security Act which would have set up the Energy Mobilization Board was cut out of the Act by an overwhelming majority in the House. The Act, as signed by President Carter, does create a Synthetic Fuels Corporation and does provide for up to $20 billion to fund synthetic fuels projects, but the "fast track" and environmental set-asides have been eliminated.

However, the Agency has been pleased by the responsiveness of the Priority Energy Project Group and Alternate Fuels Group and their various affiliates. We may no longer be under pressure to "fast track," but we have benefited greatly from the effort to look ahead and to coordinate research with regulatory activity and the generators of the emerging synthetic fuels technologies. The interchanges that have occurred over the past several months have given each participant a keener appreciation of the pressures and, sometimes subtle, details that must be mastered, which each of the other participants brings to the table. Having gained this, we are loathe to let it go.

Therefore, although the pace may not be quite as frantic as it was the first six months in 1980, we do intend to continue with the work we have started, work which has been well done.

Now that I have retraced with you the zig-zag path of legislation and administration, I can direct your attention to the much more interesting technical program that will be presented over the next four days. Thank you for coming. I am sure that you will enjoy it.

Session I: GENERAL APPROACH

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IERL-RTP PROGRAM FOR GASIFICATION AND INDIRECT LIQUEFACTION

by

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The synfuels program being conducted by the Fuel Process Branch of EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina, addresses the potential environmental impacts and control needs of coal gasification and indirect liquefaction technologies.

The purpose of this program is to support EPA's regulatory responsibilities to prevent adverse health or ecological impacts when these technologies reach commercial practice. The overall goal of this effort is to aid in the achievement of an environmentally sound and viable commercial synfuels industry.

At the start of this program, it was recognized that certain program objectives would have to be accomplished if this goal of an environmentally sound synfuels industry was to be achieved; namely:

- The characterization of the multimedia discharges from these technologies,
- The assessment of the discharges' potential health and ecological effects,
- The determination of the degree of control required to avoid adverse impacts,
- The evaluation and applicability of existing control techniques,
- The identification of new control technology needs,
- The development and/or support in the development of these new needed control processes.

In 1974, the initial program effort was directed to the development of evaluation approaches and identification of potential opportunities for data acquisition. Due to the complexity of the technologies being addressed, the lack of facilities and information, and the need to undertake broad multimedia evaluations, it was decided to develop contractual "centers of expertise." These centers would provide the technical expertise that could not be developed in-house due to limitation of personnel.

Since coal conversion technologies were only in the development stage in the U.S., and since the chemical breakdown of the coal structure results in the generation of aromatic organic compounds among which are known carcinogens, the program was based on obtaining sufficient data to identify and evaluate the total environmental effects of the discharges rather than to focus on EPA's currently regulated pollutants only.

The program was organized into four major areas:

- Environmental Assessment,
- Control Technology Development,
- Control Research Facilities,
- Methodology Development.

Environmental Assessment involves the evaluation of technologies, data acquisition, interpretation of results, projection of environmental effects, and identification of control needs.

Control Technology Development involves the evaluation of the availability and applicability of existing control technologies to meet the requirements identified by the Environmental Assessment. Additionally, operational information, reliability, and modification capabilities are evaluated. This effort has been dropped as a responsibility in the federal sector for control technology development, and demonstration was shifted to the Department of Energy.

Control Research Facilities were developed to provide information concerning the viability of control technologies and to characterize their multimedia discharges. These facilities also offer capabilities to evaluate modification of control techniques and the testing of new approaches. To date two such facilities have been constructed and are operating:

- Gasifier with gas cleaning and acid gas removal capabilities. This facility is modular and flexible in design, allowing evaluation of different systems.
- Water treatability facility to evaluate methods for treating the various wastewaters that would be generated by synfuels plants.

Methodology Department provides uniform procedures that result in consistent, cost-effective data gathering and interpretation. These procedures range from sampling/analytical techniques through data interpretation to report format. The procedures as originally developed by the

Laboratory and other EPA organizations are continually reviewed and refined.

During this initial phase of the program, considerable effort was spent in identifying availability and viability of sites for future data acquisition efforts. Due to lack of commercial U.S. facilities, plants in England, Poland, Yugoslavia, Turkey, and South Africa were surveyed for potential interest in future evaluations. These sites included the Lurgi, Koppers-Totzek, and Winkler gasification technologies.

The second phase of this program involved the actual data acquisition, interpretation of results, and identification of projected control needs. Domestically, various low Btu gasifiers were evaluated including Chapman-Wilputte, Wellman-Galusha, and Stoic. Foreign sites included a Lurgi plant in Yugoslavia and a Koppers-Totzek plant in South Africa. Results from these evaluations will be presented during this symposium. The Yugoslavian evaluation was by far the largest effort and was jointly supported and conducted by U.S. and Yugoslav experts.

The third phase of this effort which we are now well into is the compilation of data acquired to date into a data base to support EPA's guidance and regulatory activities. The Agency is now actively developing Pollution Control Guidance Documents (PCGDs) under the direction of EPA's Alternate Fuels Group. The Fuel Process Branch is involved in the PCGDs relating to low Btu gasification, medium Btu gasification, substitute natural gas, and indirect coal liquefaction.

The PCGDs will provide guidance to protect the environment during the periods preceding regulations promulgation and to avoid costly delays in the commercialization of synfuels processes due to uncertainties regarding environmental control requirements.

The primary purpose of each PCGD is to provide guidance to both system developers and permitting authorities on control approaches which are available at a reasonable cost for the technologies under consideration. The PCGDs are also intended to provide the public with the EPA's best current assessment of the environmental problems posed by the different synfuels technologies and the effectiveness and costs of available controls. This information should (a) assist system developers at the outset in their efforts to design facilities incorporating best available control technologies, and (b) aid permit reviewers in their decision making by delineating likely pollutants and their concentrations as well as available control options. The Agency intends these PCGDs to provide guidance only. The documents have no legal authority, contain no new regulations of any kind, and include nothing that is mandatory.

IERL-RTP efforts to date have shown that many data gaps still exist. Specifically, future work should address the following points:

- There is a tremendous lack of information on the effectiveness, operability, and reliability of control techniques for coal conversion plants. Information of this type needs to be gathered for the whole spectrum of potential pollutants from these plants, not just for those species for which standards or criteria exist.

- There is a need not only to demonstrate existing control techniques for their applicability to coal conversion processes, but also to initiate development of improved methods.
- There is a definite need to develop more information on the health effects of the compounds generated by the breakdown of the coal structure during gasification or liquefaction and to investigate the effects of entire discharge streams upon human health and ecological systems.

EPA/IERL-RTP PROGRAM FOR DIRECT LIQUEFACTION AND SYNFUEL PRODUCT USE

by
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The direct liquefaction program at EPA/IERL-RTP covers those synfuel processes which add hydrogen to coal and form liquid hydrocarbon products directly. The processes currently under study include SRC-II, Exxon Donor Solvent, and H-Coal. SRC-I is also included in the program because of its similarity to SRC-II even though the main product from that process is a solid. The synfuels use program covers products from coal and shale synfuel processing systems.

DIRECT LIQUEFACTION OF COAL

IERL-RTP's work in direct liquefaction of coal includes both the preparation of pollution control guidance documents, as well as involvement in support of EPA Regional Offices.

Preparation of Pollution Control Guidance Documents

Laboratory-prepared EPA pollution control guidance documents are intended to be used by EPA Regions as they evaluate permits, by EPA regulatory offices as they prepare formal regulations, and by process developers as an indication of the extent of pollution control EPA considers appropriate for the evolving synfuel industry.

The documents contain extensive descriptions of the processes and pollutants discharged, and detailed descriptions of control devices that might be applied to various sources. Where appropriate, process design modifications are proposed if they would result in an environmentally and economically more attractive system.

The range of pollutants considered for control includes those currently regulated, as well as those unregulated where chemical and bioassay test data indicate control would be prudent. Synfuel products are also considered in the document to the extent that their on-site storing and handling impacts on the local environment.

IERL-RTP is making every effort to ensure that the best information available is contained in the guidance documents. A work group has been established which has representatives from all EPA's regulatory offices. The Regions are also represented. Representatives from DOE and the process developers in industry participate by providing data and a critical technical review of the accuracy of the technical components of the guidance documents. Extensive reviews, both internal and external to EPA, are planned. Participants will include all regulatory offices, the EPA Science Advisory Board, environmental groups, industry, DOE, and the general public.

The schedule of activities for the next 2 years is shown in Figure 1. The first version of the guidance document will be heavily slanted toward SRC-II. This emphasis is the result of a paucity of data available from the H-Coal and Exxon Donor Solvent (EDS) pilot plants. The guidance document is expected to be updated to reflect up-to-date information on EDS and H-Coal.

Regional Support Activities

The second important use of guidance documents is as an aid to EPA Regional Offices as they evaluate permit applications. Regions III and IV have, or will shortly receive, Prevention of Significant Deterioration (PSD) applications for SRC-II and SRC-I, respectively. They also have received and been asked to comment on Environmental Impact Statements for these two processes. Since the guidance documents are not yet available to the Regions, IERL-RTP is providing ad-hoc assistance in the evaluation of permit applications and the review of impact statements.

Inputs provided to date have been mainly identification of data deficiencies in the applications or impact statements. In limited cases, where specific control technologies have been identified by DOE, sufficient background material has been pulled together to make an analysis of the appropriateness of the DOE selection. Evaluation of specific control systems has generally not been the

FIGURE 1

DIRECT LIQUEFACTION POLLUTION CONTROL GUIDANCE

DOCUMENT SCHEDULE

ACTIVITY MILESTONES	Date	1980								1981												1982								
		May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Program Kickoff	6/12/80		▲																											
Draft chap. on Source Assessment	10/31/80						▲																							
Draft chap. on Control Technology Options	1/15/81									▲																				
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Second Draft Vol. I-III to AFG, SAB, DOE, IRC	9/ 7/81																	▲												
Receive comments on 2nd Draft	10/26/81																		▲											
Review AFG/SAB/DOE comments with DLWG	11/ 6/81																			▲										
Third Draft Vol. I-III to DLWG/AFG/SAB	1/15/82																					▲								
Third Draft Vol. I-III to EPC	1/31/82																					▲								
Revise Third Draft, to DLWG/AFG	3/ 1/82																							▲						
Federal Register Notice of Public Forum	3/15/82																							▲						
Public Forum	5/15/82																									▲				
Receive Public Comments	6/15/82																										▲			
Review Public Comments with DLWG	7/ 1/82																											▲		
Recommend Comment incorporation to AFG	7/15/82																											▲		
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Final PCGD to OEET/DLWG/AFG/DOE/EPC	9/ 1/82																													▲
Transmit to printer with EPC approval	9/15/82																													▲

Abbreviations:

DLWG - Direct Liquefaction Working Group
OEET - Office of Environmental Engineering & Technology
IRC - Industrial Review Committee
AFG - Alternate Fuels Group
SAB - Science Advisory Board
EPC - Energy Policy Committee

prime task, however, because DOE has not progressed very far with detailed specifications for control technology components of the SRC-II system.

West Virginia personnel are being assisted in their evaluation of a construction permit request from DOE. The same problem occurs here: it is difficult, if not impossible, to estimate the effectiveness of the environmental control system when it has not been specified in sufficient detail. These ad-hoc support activities are expected to continue indefinitely. As a matter of routine, all inputs to Regions and States are channeled to EPA's regulatory offices for comment.

IERL-RTP expects to continue its direct liquefaction assessment program for several years. Major items of concern which have been identified and will be investigated include the nature and toxicity of emissions from heavy ends processing, the feasibility of zero discharge water systems, the determination of the toxic and leachability characteristics of gasifier solid wastes, and factors which affect stream time for sulfur cleanup systems. IERL-RTP expects to spend about $2 million per year in this assessment and control technology evaluation area.

SYNFUELS USE PROGRAM

EPA's Synfuels Use Program has been underway for approximately 6 months. For the past few years much emphasis has been placed on determining the environmental impact of synfuel production facilities. That is certainly a worthwhile objective but it is clear that, at least in the near term, the most significant human exposure to synfuel related materials will come from the transport, storage, and use of the products. Very little attention has been given to this important aspect of the evolving synfuels industry. The major objective of the program is to estimate the human exposure associated with various uses of synfuels and to estimate the toxicity of the materials to which people are exposed. These estimates are of considerable importance to EPA's Office of Pesticides and Toxic Substances as they make decisions related to the application of the Toxic Substances Control Act to the synthetic fuels industry.

To date IERL-RTP has completed a rough-cut market penetration projection for the various synthetic fuels. The study was limited to coal and shale oil products because of their nearer term probability for development and uncertain environmental status. This market penetration projection is complemented by a summary of all completed and on-going human effects research programs which deal with synthetic fuels. An analysis of these two studies, planned for this Fall, will result in a specification of the types of data still needed to allow estimation of the risk associated with exposure resulting from synfuels use. Priorities for completing the effects work will be established based on the exposure estimates and estimates of the toxicity of the materials in question: materials of higher exposure or higher toxicity will be given top priority. These data requirements and priorities will be sent to DOE, synfuels developers, and EPA research laboratories with recommendations for implementation. All the effort on risk estimation has been closely coordinated with EPA's regulatory offices. It is very important that the data generated be of the quality and type that is directly useable for the formulation and promulgation of regulations.

EPA's Synfuels Use Program over the next few years will continue to evaluate the evolving synfuels industry especially from the view of risk to human health from new uses of the products or new ways of incorporating synfuels into the existing production system; for example, blending of synthetic and natural crude oil in refineries. One current major deficiency is that very little effects work is underway to evaluate the toxicity of synfuel combustion products. As these problems become more well defined, IERL-RTP will be conducting research to reduce the severity of the impact of the use of these products. IERL-RTP will also begin to look at other environmental impacts such as ecological effects, regulatory options that are available for dealing with the problems of synfuel use, and synfuels that are preferable for development from social, economic, and environmental points of view. IERL-RTP's budget for this program is approximately $1 million per year for the next 5 years.

UPDATE OF EPA/IERL-RTP ENVIRONMENTAL ASSESSMENT METHODOLOGY

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Abstract

EPA's IERL-RTP has developed a systematic approach for performing each aspect of environmental assessment to allow for consistent data gathering and interpretation. Environmental assessment requires the determination of contaminant levels associated with point source discharges and comparison of those determinations with target control levels. Procedures for conducting phased environmental assessments involving Level 1 and Level 2 chemical analyses and bioassays have been formalized. Multimedia Environmental Goals (MEGs) reflecting potential toxicity of specific chemicals provide the target values used for comparison. Source Analysis Models (SAMs) delineate discharge stream severities based on the components present and mass flow rates. The Level 1/Level 2 chemical analysis approach has been coupled with the categorical system for organizing chemicals addressed by MEGs.

The computerized Environmental Assessment Data System (EADS) at IERL-RTP is used to store environmental assessment data and to provide links between characterization and target goals. Eventually, EADS will be used to automate large portions of the assessment data analysis.

UPDATE OF EPA/IERL-RTP ENVIRONMENTAL ASSESSMENT METHODOLOGY

INTRODUCTION

In support of the Environmental Protection Agency's standards-setting and regulatory functions, information is needed in response to the question, "To what extent does a particular industrial source cause pollution damage to the environment?" Answers to this question involve a complex mix of information from numerous scientific and engineering disciplines. To provide a structured and cost-effective approach to assembling and interpreting this information, the concept of an environment assessment has been developed and procedures established for its implementation.

An assessment of the pollution potential of an industrial source is necessarily complex because it addresses many types of industrial discharges into all environmental media (air, water, land). The approach to environmental assessment developed by the EPA's Industrial Environmental Research Laboratory at Research Triangle Park, N.C., is to divide the work to be accomplished into discrete steps with the results of each completed phase providing guidance for succeeding efforts. Four main advantages of such a formal approach are that:

1. Thorough screening ensures coverage of potential problems identifiable on the basis of the existing effects data.
2. Attention is focused on the chemical constituents of highest concern.
3. Many unnecessary samples and analyses are eliminated by virtue of the guidance provided by the results of previous phases.
4. Results obtained from different sources by different investigators are directly comparable.

IERL-RTP began to develop this structured approach to environmental assessment about 5 years ago. By then, the need for a common methodology was recognized clearly, for experiences since 1969 with Environmental Impact Statements (required under the National Environmental Policy Act) had already demonstrated the wide variation of outputs that could occur in assessing possible environmental impacts. Predictably, when the first specific procedures and practices to be followed in environmental assessment were spelled out in an IERL-RTP report in 1976[1], the approach was met with considerable resistance from contractors. Some of that continues, but the advantages of a common methodology are becoming more apparent as the volume of collected data grows. Over the last 4 years, numerous modifications and additions have been made in the various segments of the methodology as a result of continuous research and in response to comments from the users. In many cases, those applying the procedures are also the methodology developers since the development of the methodology has proceeded concurrently with its implementation in the preliminary environmental assessments conducted by IERL-RTP. Although the evolution of the methodology continues, the overall approach appears to be accomplishing its initial objectives.

Many of the conclusions that will be presented in papers at this symposium will be expressed in terms defined by the IERL-RTP environmental assessment methodology. Because of the common approach, results from the different studies are comparable, even though certain specific procedures vary to accommodate unique problems encountered in each assessment program. This paper describes briefly the IERL-RTP environmental assessment methodology and its various components at their present level of development. It is hoped that this presentation will contribute to a better understanding of the specific technology assessments.

APPROACH

There are five major components of the IERL-RTP environmental assessment methodology:

- Technology background development
- Sampling and analysis
- Environmental goals
- Impact analysis
- Control technology evaluation

Three levels of effort are defined for data acquisition involving sampling and analysis. Level 1 was designed for initial screening or survey of potential pollutants, and its goal is the comprehensive survey via chemical and bioassay analyses of all discharges to the environment. Chemical analyses at this level are primarily directed toward the identification and semiquantitation of categories of compounds present in the discharge streams. Level 2 focuses on the streams and compound classes found to be of major concern in Level 1. Analyses are aimed at identifying and quantifying the specific chemicals present. Level 3 is presently in the conceptual planning stage, and will involve selectively monitoring the pollutants of concern identified in Levels 1 and 2 and determining their variation with time and process operating conditions. Evaluation of the effectiveness of pollution control devices in place at the test site would be a product of Level 3 data collection.

TECHNOLOGY BACKGROUND DEVELOPMENT

Much can be learned about probable pollution problems associated with a given process or technology by reviewing existing information and applying scientific and engineering experience. Consequently, the first step in an environmental assessment is to obtain all the pertinent literature available. Attention is given to the current and projected status of the commercial development of the technology, the varieties of process units applicable, the process chemistry, and the nature, quantities and points of discharge of waste streams and fugitive emissions (leaks, spills, etc.). Such literature reviews usually reveal information gaps that render difficult or impossible an adequate determination of the pollution potential of the technology and associated environmental damage. Both the selection of the facilities to be tested and the determination of the amount and types of data to be collected are directed by the information derived from the literature review.

Once a particular facility has been selected as a test site, a detailed engineering evaluation of existing data for that facility is made, and tentative sampling points are selected. Plant layout, temperatures, pressures, flow rates, and other plant operation data are obtained in a pretest site survey. The final test plan states what, how, and when required sampling and analysis activities will be performed. It informs the sampling crew of optimum sampling locations and conditions and of unusual circumstances that may be encountered during the sampling process. Sample preservation techniques and procedures for handling and shipment of samples are also discussed.

SAMPLING AND ANALYSIS--LEVEL 1

Sampling and analysis procedures for Level 1 environmental assessments are set forth in the second edition of the IERL-RTP Procedures Manual.[2] This manual supersedes the 1976 manual. Although the overall approach to sampling and to organic and inorganic analysis at Level 1 remains unchanged since 1976, incremental changes in the procedures have vastly improved their effectiveness and reliability. In accordance with a guideline issued by IERL-RTP, all IERL-RTP contractors and grantees performing environmental assessments are required to use the procedures in the revised manual. The manual addresses quality control/quality assurance as well as the specific analytical and sampling techniques to be used. New developments in the areas of sampling, analysis, and quality control are reported in a quarterly report called "Process Measurements Review." This widely circulated publication of the Process Measurements Branch of IERL-RTP announces revisions in the procedures manual as they are adopted.

It should be emphasized that the objective of Level 1 data acquisition is to provide a data base to allow prediction of the pollutants and streams of concern. Once this data base is in place, as it is presently for coal-fired power plants, it is appropriate to pursue Level 2 investigations. Thus, a complete site-specific Level 1 study need not precede every Level 2 effort. However, even for well-developed bases, occasional Level 1 or partial Level 1 surveys can prove informative[3].

Level 1 Sampling

Level 1 sampling programs are designed to permit efficient collection of all substances in a stream, making maximum use of existing stream access sites. Samples from each process feed stream and each process effluent stream must be provided for the Level 1 assessment. Multimedia sampling strategies are organized around five general types of samples: (1) gas/vapor, (2) particulates/aerosols, (3) liquids/slurries, (4) solids, and (5) fugitive emissions. Particulate from gas streams is sized (four fractions recovered) in the operation employing the Source Assessment Sampling System (SASS). The availability of the Fugitive Ambient Sampling Train (FAST) has improved the collection of airborne fugitive emissions. Specifics of the operation of the SASS and the FAST are discussed in the second edition of the Procedures Manual.

Sample size requirements for Level 1 are established to ensure that analytical results will supply meaningful data. Procedures and equipment to be used for various stream types are also specified. Table 1 indicates the

TABLE 1. GUIDELINES FOR LEVEL 1 STREAM SAMPLING [2]

STREAM	SAMPLE SIZE	LOCATION	SAMPLE PROCEDURE
Vapors with or without particulate	30 m^3	Ducts, stacks	SASS train
Liquid	20 L*	Lines or tanks	Tap or valve sampling
		Open free-flowing streams	Dipper method or composite sampler
Solids	1 kg	Storage piles	Coring
		Conveyors	Full stream cut
Gas (reactive) organic material with bp $< 100°$ C; N and S species	2 L	Ducts, stacks, pipelines, vents	Grab sample (glass bulb)
Gas (fixed) O_2, N_2, CO_2, and CO	10-30 L	Ducts, stacks, pipelines, vents	Integrated bag sample
Fugitive emission	2,496 m^3	Ambient atmosphere	FAST or modified hi-vol

*May need additional sample volume depending on the nature of the biotesting employed.

IERL-RTP guidelines for Level 1 stream sampling based on the detection limits of the analytical techniques subsequently employed.

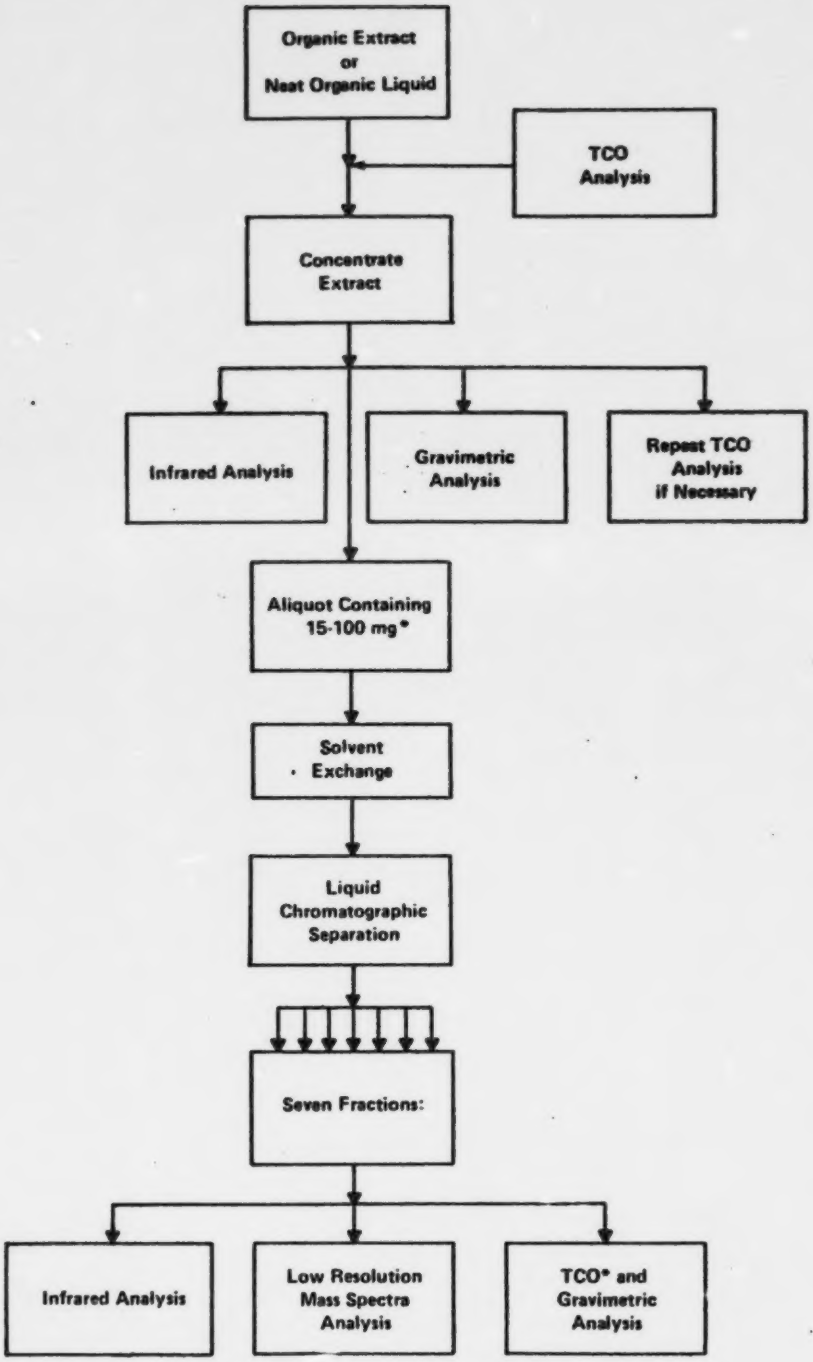
Level 1 Chemical Analysis

Samples collected from a facility are subjected to a Level 1 chemical analysis designed to characterize both organic and inorganic constituents. Solid samples may also receive a morphological examination. The objective of Level 1 organic analysis is to isolate and semiquantitate (accurate to within a factor of three) the predominant classes of organic compounds present in a given sample. Figure 1, adapted from Reference 2, depicts the current procedure set forth for Level 1 organic analysis. Quantitative information is provided by gas chromatography (total chromatographable organics, TCO) and by gravimetry (GRAV). Qualitative and semiquantitative information is obtained from conventional liquid chromatography (LC), infrared spectrometry, and low resolution mass spectrometry (LRMS). A liquid chromatographic separation based on polarity is employed, which results in seven fractions. Categories of chemicals expected to elute in each fraction are recognized, and this information is used in interpreting the LC data.

Inorganic species determined in the Level 1 program include certain inorganic gases; the major, minor, and trace elemental constituents; and selected anions. Inorganic gases are measured at the test site using gas chromatographic, spectrometric, and titrimetric methods. Elemental and ion determinations are performed on both solid and liquid samples in an off-site laboratory. Ion chromatography or commercial test kit procedures are employed for ion determinations. Elemental analysis is accomplished by spark source mass spectrometry (73 elements) and atomic absorption spectrometry (for mercury). It is recognized that analyses by spark source mass spectrometry are better for some elements than for others, but for Level 1 screening purposes the technique is sufficient. More precise determinations may be provided at Level 2.

Level 1 Biological Analysis

While chemical characterization of a sample identifies known hazardous chemicals, biological tests provide complementary information for mixtures whose health/ecological effects are unknown. Biological tests conducted in a Level 1 effort involve short-term screening tests designed to determine the


Organic Extract
or
Neat Organic Liquid
TCO
Analysis
Concentrate
Extract
Infrared Analysis
Gravimetric
Analysis
Repeat TCO
Analysis
if Necessary
Aliquot Containing
15-100 mg*
Solvent
Exchange
Liquid
Chromatographic
Separation
Seven Fractions:
Infrared Analysis
Low Resolution
Mass Spectra
Analysis
TCO* and
Gravimetric
Analysis

*If less than 15 mg is recovered, go to LRMS.

Figure 1. Organic analysis methodology.[2]

health-related and ecological effects of the samples.[4,5] The tests to indicate potential health-related effects include the use of both in vitro and whole animal bioassays designed to detect evidence of any toxic or mutagenic response in the test organisms. Ecological tests measure the response of aquatic and terrestrial organisms to the pollutants and include the use of algae, vertebrate and invertebrate animals, land plants, and insects. The revised Level 1 Bioassay Procedures Manual is expected to be made available this Fall from EPA. The specific bioassay tests used in Level 1 screening are indicated in Table 2, updated from Reference 5 to reflect the current bioassay protocol procedures from the revised manual.[6]

The bioassays for Level 1 screening constitute a minimum set of cost-effective tests to evaluate the potential biological effects of a sample. The tests were chosen after extensive evaluation and validation and reflect experience in three pilot studies and other selected applications.

INTERPRETATION OF LEVEL 1 DATA

In the phased approach to environmental assessment, Level 1 test data need to be interpreted so that pollutant categories and waste streams can be evaluated with respect to their potential environmental insult. Such an interpretation of the data will lead to a decision as to what Level 2 tests, if any, should be conducted to better characterize the problem streams. In order to perform this evaluation, it is necessary to have a set of environmental criteria against which the chemical test data can be compared. Criteria which have been developed for this task are referred to as Multimedia Environmental Goals (MEGs).[7,8,9] The procedure designed to guide the systematic interpretation of Level 1 chemical analysis involves a source analysis model called SAM/IA introduced in 1977.[10] (A revised version of SAM/IA is expected to be available in Spring of 1981.[11]) Interpretation of bioassay data has also been systematized using rankings of responses from the various tests performed.

Two major outputs desired from a Level 1 test effort are (1) the ranking of pollutant classes within a stream and (2) the ranking of discharge streams. Both rankings are based on potential adverse environmental effects.

TABLE 2. LEVEL 1 SCREENING BIOASSAYS

HEALTH EFFECTS TESTS

TEST	EFFECT	DESCRIPTION	TEST OUTPUTS
Microbial Mutagenesis (Ames Test)	Mutagenesis	Genetically sensitive strains of microorganisms are exposed to various doses of sample with and without metabolic activation.	Mutagenic response is measured relative to controls.
Cytotoxicity	Cellular Toxicity	Selected cells (RAM, CHO, or WI-38) are exposed to various doses of sample, then various endpoints are measured.	An index of functional impairment, toxicity, and metabolic change is established relative to controls.
Rodent Acute Toxicity (RAT Test)	Whole Animal Toxicity	Rats or other rodents are fed a quantity of sample, then observed daily for adverse symptoms over a 14-day period. The experiment is terminated with a necropsy exam.	Inventory of pharmacological and gross physiological effects in a whole animal system.

ECOLOGICAL EFFECTS TESTS

TEST	EFFECT	DESCRIPTION	TEST OUTPUTS
Algal Growth Response	Algal Growth Inhibition or Promotion	Cultures of selected marine and/or freshwater algae are used to gauge reaction to sample or dilution thereof.	Growth response measure—stimulation or inhibition.
Aquatic Animal Exposure (Static Acute Bioassay)	Toxicity to Fish or Daphnia	Select marine and/or freshwater fish and Daphnia are exposed to a graded dilution series of samples.	Gross index of toxic potential to representative animals.
Plants (Stress Ethylene and Root Elongation)	Stress or Toxicity to Plants	Tests in these three areas are being evaluated.	Effects on plants.
Insect	Toxicity to Drosophila		Effects on insects.
Bioaccumulation	Potential Accumulation	HPLC procedure for evaluation of occurrences in fatty tissue.	Number of components that accumulate. Accumulation potential of each component.

Multimedia Environmental Goals (MEGs)

MEGs are chemical-specific goals expressed as concentrations in air, water, and land (or solid waste). Separate values reflect potential human health effects and potential ecological effects. Two types of MEGs are distinguished--ambient goals (AMEGs) and discharge goals (DMEGs). AMEGs are target concentrations of individual chemical species in the ambient environment to which receptors (i.e., human populations or ecological systems) may be exposed on a continuous, long-term basis. DMEGs represent target concentrations for contaminants in undiluted waste streams. It is assumed that receptors would be exposed only for short intervals to DMEG concentrations.

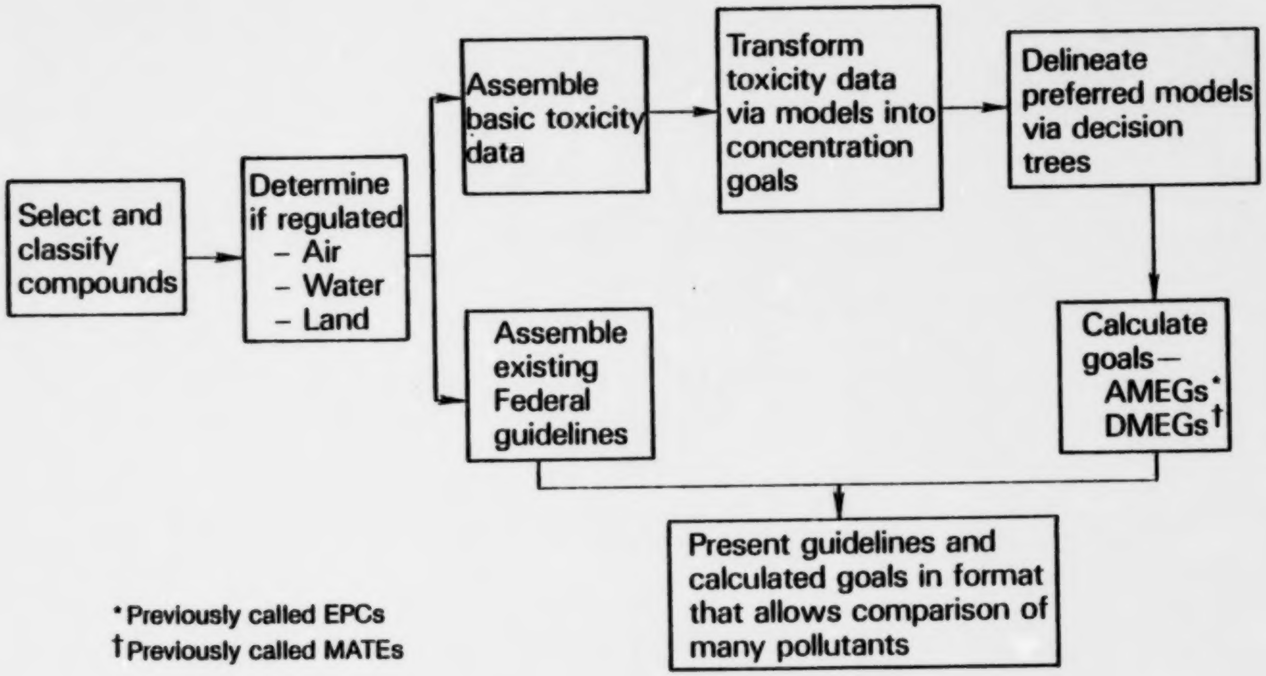
Chemicals for which Federal standards or guidelines have already been established or proposed are assigned MEG values reflecting the most stringent standards or guidelines. Otherwise, both AMEGs and DMEGs are derived from available toxicity data. Simple mathematical models based on worst-case assumptions are used to transform the raw data into the needed concentration goals for air-, water-, and land-based pollutants. The approach used to generate MEGs for chemical pollutants is illustrated in Figure 2.

Background information is compiled for each chemical and supplied with the recommended set of MEG values. MEGs have been established for approximately 600 chemical substances, and the list is continually updated and expanded. Chemicals addressed by MEGs are grouped in pollutant categories to facilitate their use in Level 1 data interpretation (since Level 1 data are expressed as chemical categories quantified in each LC fraction).

It should be emphasized that the development of MEGs is not related to Standards setting. MEGs are established as criteria for interpretation of environmental assessment data, which necessitates ranking a large number and variety of chemicals, including many nonregulated pollutants.

Source Analysis Model, SAM/IA

To rank the pollution potentials of components within a single stream, one compares the measured stream concentrations to respective DMEG values. A difficulty is that DMEGs are species-specific, whereas Level 1 generally reports only the concentrations of categories of compounds. To circumvent this problem, the entire concentration of a class of compounds found to be present is compared to the lowest DMEG for a chemical in that category. This ratio is called the discharge severity (DS) of the component.


Select and classify compounds
Determine if regulated
– Air
– Water
– Land
Assemble basic toxicity data
Assemble existing Federal guidelines
Transform toxicity data via models into concentration goals
Delineate preferred models via decision trees
Calculate goals—
AMEGs*
DMEGs†
Present guidelines and calculated goals in format that allows comparison of many pollutants

*Previously called EPCs
†Previously called MATEs

Figure 2. Approach for chemical pollutant MEGs.

$$DS_i = \frac{\text{(component concentration in stream)}}{\text{DMEG}}$$

If good scientific evidence exists to eliminate the most hazardous species from consideration, the next most hazardous species is selected, and so on. In general, components or classes of compounds with discharge severities greater than unity are considered environmentally significant. Repeating this procedure for every category of chemicals found in the stream allows the ranking of these categories on the basis of potential environmental damage. Discharge severities for all components are summed to give a total discharge severity (TDS) for the stream.

$$TDS = \Sigma DS_i$$

In comparing the potential environmental harm of different waste streams using the DS approach, both the stream compositions and mass flow rates must be considered. Therefore, a total weighted discharge severity (TWDS) is defined as the product of the stream mass flow rate and the summation of the component DS_is in the stream.

$$TWDS = \text{(stream mass flow rate)(TDS)}$$

Comparison of the TWDS for different streams that are of the same medium allows comparison and ranking of the streams on the basis of potential environmental insult. Streams with high TDS levels and those that are ranked high using the TWDS as criteria are candidates for Level 2 sampling and analysis.

Bioassay Data Interpretation

Further indication of the potential environmental harm associated with a waste stream is supplied by the biological tests. In Level 1 these tests are short-term bioassays for the detection of acute biological effects. Evaluation of these data is based on the maximum applicable dose for each biological test; i.e., the maximum amount of a substance which can be administered in a given bioassay due to experimental limitations. Test results are ranked as high, moderate, low, or nondetectable biological responses. Table 3 (taken from Reference 5) gives the response ranges and maximum applicable doses for several of the Level 1 bioassays. A positive Ames test or toxic responses from any two other tests suggest a need for Level 2 information. To aid in the interpretation of the bioassay data , IERL-RTP released a report on data formatting for Level 1 in April 1979.[12]

TABLE 3. RESPONSE RANGES FOR RANKING OF VARIOUS BIOTESTS[5]

ASSAY	ACTIVITY MEASURED	MAD	RESPONSE RANGES			
			HIGH	MODERATE	LOW	NOT DETECTABLE
Health Tests						
Ames	Mutagenesis	5 mg/plate or 500 μL/plate	$<$0.05 mg or $<$5 μL	0.05-0.5 mg or 5-50 μL	0.5-5 mg or 50-500 μL	ND at $>$5 mg or ND at $>$500
RAM, CHO, WI-38	Lethality (LC_{50})	1,000 μg/mL or 600 μL/mL	$<$10 μg or $<$6 μL	10-100 μg or 6-60 μL	100-1,000 μg or 60-600 μL	$LC_{50} >$ 1,000 μg or $LC_{50} >$ 600 μL
Rodent	Lethality (LD_{50})	10 g/kg or 10 mL/kg	$<$0.1	0.1-1.0	1-10	$LD_{50} >$ 10
Ecological Tests						
Algae	Growth Inhibition (EC_{50})	1,000 mg/L or 100%	$<$20% or $<$200 mg	20-75% or 200-750 mg	75-100% or 750-1,000 mg	$EC_{50} >$ 100% or $EC_{50} >$ 1,000 mg
Fish	Lethality (LC_{50})	1,000 mg/L or 100%	$<$20% or $<$200 mg	20-75% or 200-750 mg	75-100% or 750-1,000 mg	$LC_{50} >$ 100% or $LC_{50} >$ 1,000 mg
Invertebrate	Lethality (LC_{50})	1,000 mg/L or 100%	$<$20% or $<$200 mg	20-75% or 200-750 mg	75-100% or 750-1,000 mg	$LC_{50} >$ 100% or $LC_{50} >$ 1,000 mg

MAD = Maximum Applicable Dose (Technical Limitations)
LD_{50} = Calculated Dosage Expected to Kill 50% of Population
LC_{50} = Calculated Concentration Expected to Kill 50% of Population
EC_{50} = Calculated Concentration Expected to Produce Effect in 50% of Population
ND = Not Detectable

Streams ranked relatively high in potential adverse health or ecological effects on the basis of chemical composition do not always exhibit a highly positive biological response in the Level 1 bioassay battery and vice versa. This is because the DMEGs may be based on biological responses different from those measured in the bioassays. Also, possible synergistic and antagonistic effects occurring in complex mixtures of substances are often characteristic of waste streams; these effects are not taken into account by the MEG/SAM approach, which assumes that toxic effects of compounds are additive. Therefore, chemical tests and biological assays complement each other and should be run in parallel. The decision to proceed with Level 2 data acquisition should be made on the basis of all available chemical and bioassay information. Later this fall, IERL-RTP's Process Measurements Branch will issue a comparison of the sensitivities of bioassay tests and chemical analyses.[6]

SAMPLING AND ANALYSIS--LEVEL 2

Level 2 sampling and analysis is dictated whenever Level 1 chemistry or bioassay indicates a possible hazard. Level 2 inquiries are directed at the confirmation of Level 1 results and at the identification and quantification of specific compounds whose presence was inferred from the Level 1 categorical analysis.

Level 2 generally requires a sampling and analysis scheme specifically tailored to address questions raised by a Level 1 investigation. The appropriateness of a Level 1 sample or sample extract for a more detailed Level 2 study must be carefully evaluated. Was the Level 1 collection efficiency high enough for the species in question? Is the substance to be analyzed sufficiently stable so as to render still valid the original Level 1 sample? Is the Level 1 sample truly representative of the source over a reasonable timeframe? Would an alternative sampling procedure provide a more interference-free sample? Upon consideration of these and similar concerns, the decision may be made to return to the test site for a second sampling effort. While such a Level 2 sampling effort may be expected to provide more rigorous attention to detail, it generally will not be as extensive as in Level 1 due to the elimination of certain streams and compound classes from consideration.

Level 2 Chemical Analysis

It is not possible or practical to formalize a single effective analytical scheme for Level 2 since each question to be answered at this stage represents a unique case. Analytical methods and/or instruments may be used which are capable of greater selectivity and sensitivity than those employed in Level 1. Procedures manuals addressing organic and inorganic sampling and analysis have been issued by IERL-RTP to serve as guidelines for Level 2 data acquisition.[13,14,15]

Refinement of the Level 2 chemical methodology continues. A document prepared by A.D. Little, Inc., on Level 2 Organics Analysis Applications, soon to be released by IERL-RTP, reports on the validation of Level 2 procedures on actual samples. Also, IERL-RTP will soon issue a report on interpretation of LRMS data, which is intended as an aid for the spectroscopist.[3]

Level 2 Biological Analysis

In some cases, Level 2 biological tests may be as simple as those in Level 1. Other cases may require more elaborate and classical methods. A Level 2 biological test protocol is being developed, which will include subacute and chronic effects and/or fractionation of samples for verification and quantification of results from the Level 1 screening studies.[6]

Interpretation of Level 2 Results

Level 2 analytical results may be interpreted by several different protocols. The usual method is simply to recalculate for each stream the component discharge severities (DS_i) and the total weighted discharge severity (TWDS) using the component-specific information now available. Such an iteration may confirm the Level 1 results or may sufficiently alter the DS and TWDS values to rank the components or streams of major concern differently.

Because Level 1 data are obtained for rapid screening purposes, no effort is made to consider the dispersion of the various waste streams into the ambient environment. At Level 2, such considerations are desirable to better assess the environmental impact of potentially significant streams. Thus, a second method for interpreting Level 2 data involves estimation of the ambient concentration of a chemical, which would result from a particular source stream, and comparison of that ambient level with the AMEG for the chemical.

A Source Analysis Model, SAM/IA, is being developed to relate Level 2 source test data to AMEGs.[11] This approach represents a degree of refinement above the comparison involving DMEGs in that AMEGs are based upon continuous receptor exposures to individual chemicals in the ambient environment. DMEGs represent goals for short-term exposures, and the use of the SAM/IA approach assumes that human or ecological receptors will come in contact with undiluted discharge streams.

The component-specific data acquired by Level 2 sampling and analysis and the interpretation of that data using either of the SAM models thus provide a reasonable basis upon which to assess the environmental impact of a source. Discharges unsatisfactory from a health/ecological standpoint are readily identified so that appropriate pollution control devices may be recommended.

For developing industries, such as synfuels, Level 2 data may be applied in formulating guidance recommendations for permit writers and developers. Level 2 data may influence standards-setting for existing industries, or the data may trigger Level 3 investigations.

EFFECTIVENESS OF THE APPROACH

Assessments of several technologies have been completed using the Level 1/Level 2 methodology. These studies, directed toward the textile industry, ferroalloy processes, conventional combustion, fluidized bed combustion, low-Btu gasification, and other technologies, have been performed by different contractors. The results of the analytical tests, however, may be compared readily because samples were obtained by similar methods and similar laboratory procedures were followed. Also, the analysis data are compared to a similar basis; i.e., the MEGs. Common formats for reporting of assessment results have simplified the comparison of results from different sources.

The Level 1/Level 2 phased approach to data acquisition has been compared to the direct approach for environmental assessment of particulate-laden flue gases. The Level 1 techniques were shown to be effective in narrowing the scope of the investigation with quantitative Level 2 determinations being directed toward the samples and components of highest environmental significance. It was shown that the cost of the phased approach can be on the order of 75 to 50 percent of the cost of the direct approach.[16] The thorough screening provided at Level 1 ensures that problem streams or components do not go undetected.

DATA MANAGEMENT

A data management system is imperative for storing, editing, updating, and retrieving the vast amount of source test data generated by environmental assessment projects. To this end, IERL-RTP has developed the Environmental Assessment Data Systems (EADS) stored in the UNIVAC computer at EPA's Environmental Research Center in North Carolina. The EADS is a comprehensive system of computerized data bases that describe multimedia discharges from energy systems and industrial processes. The data bases are interlinked across media and across industries.[17]

The EADS serves to (1) consolidate the increasing volume of environmental data, (2) provide uniform data protocols, and (3) maintain current information in a readily accessible mode. Four media-specific waste stream data bases are included to address fine particle emissions, gaseous emissions, liquid effluents, and solid discharges. A fifth data base for multimedia fugitive emissions will be added next year. These data bases are designed to permit entry and retrieval of information pertinent to specific tests, sources, processes, control devices, or specific pollutants. Coding forms for data entry are designed to accommodate results from Level 1 and Level 2 chemical and biological analyses.

In addition to the waste stream data bases, there are currently two important reference data bases within the EADS. These are MEGDAT, which stores MEG values and supporting information for MEGs pollutants, and the Chemical Data Table which contains names, synonyms, CAS registry numbers, and MEG ID numbers for almost 2,000 chemicals. A Quality Assurance/Quality Control reference data base for laboratory audit data is projected to be in place in EADS in 1981. An additional reference data base called the Project Profile System will be linked with the EADS soon. This system presently contains profile information from conventional combustion projects but is also designed to manage data from other technology areas.

EADS is expected to provide essential data to several EPA programs, including:

- Environmental Assessment Programs
- Inhalable Particulate Standards Development

- Wastewater Treatability Manual Development
- Evaluation of Control Technology Alternatives
- Industrial Boiler NSPS
- Identification of Hazardous Pollutant Emissions
- Radionuclide Correlations with Particle Size

An IERL-RTP directive, dated May 1978, requires that all sampling and analysis data obtained under IERL-RTP source sampling contracts awarded after June 30, 1978, be entered in the appropriate EADS data base. User's manuals for the existing data bases are available, and specific information requests will be filled by the EADS Manager at IERL-RTP.[17]

Quality Assurance and Control

Agency policy requires participation by IERL-RTP in a centrally directed Quality Assurance Program for monitoring and measurement efforts. The Quality Assurance Plan developed for IERL-RTP fulfills one requirement under the overall program managed by EPA's Quality Assurance Management Staff, Office of Monitoring Systems and Technical Support. The plan is expected to become effective October 1, 1980.[18] Provisions in IERL-RTP's Plan specify that all measurement and monitoring data collected should be of known and documented quality. Throughout the sampling and analysis segments of any environmental assessment, a program of quality control and quality assurance must be followed to ensure the desired accuracy and precision of results. The quality of the data must be acceptable for its intended use. Analytical methods and procedures should conform to EPA approach methodology when appropriate. Customary requirements of good laboratory practice (including preservation of samples, standardization of reagents, and calibration of equipment) must be verified and documented. An independent group working in cooperation with the laboratory personnel may review the laboratory's methods, engage in on-site inspections, provide blind samples for analysis, and duplicate the sample analyses to confirm results obtained by the test laboratory. Audited each year will be 10 to 20 percent of the projects within IERL-RTP.

CONTINUED DEVELOPMENT TRENDS

The phased environmental assessment approach described here has been undergoing continual development since its inception in 1976. The various components of the methodology have been and continue to be subjected to critical review from both inside and outside the Agency. A major peer level review involving 15 panelists was held in January 1979.[19] As a result of such reviews, on-going research at IERL-RTP, and from user comments, refinements continue in the sampling/analysis procedures, data reporting formats, MEGs development, SAM models for data interpretation, nomenclature, bioassays, and mechanisms for data management.

Areas designated for significant future development include:

1. Although the MEGs methodology makes use of most types of readily available toxicity data, the models involve many assumptions and extrapolations. Substantial refinements in the MEGs methodology are planned for Phase II MEGs. Among the modifications will be (a) adoption of the EPA Carcinogen Assessment Group approach for relating concentrations of potential carcinogens to the resulting level of risk in the exposed population; (b) methods to address accumulation and bioconcentration; (c) category-specific models for utilizing animal data; (d) better use of inhalation data; and (e) improved, category-specific models to generate values for solid waste. A review of the Phase II methodology by the EPA Science Advisory Board is being scheduled for 1981.

2. Research is being initiated on health and ecological effects for both individual chemical substances and complex mixtures for which inadequate data exist to derive MEGs. As results of these tests become available, they will be incorporated in chemical information summaries and will serve as the basis for new MEGs values.

3. Efforts are underway to improve models for predicting risks to human health or to the ecology as a function of exposure to hazardous chemicals. Such models will be incorporated in MEG as data for their implementation becomes available.

4. Development of MEGs to account for skin absorption is being considered.

5. Regional and site-specific models are needed to describe the transport of pollutants from point of discharge to receptors in the ambient environment. Transformation models are also needed for use in more sophisticated SAMs.

6. The current environmental assessment methodology does not include evaluation of water parameters such as hardness, total dissolved solids, BOD,

and COD. Because these parameters contribute to the environmental significance of waste streams, MEG values are needed.

7. Level 3 sampling and analysis methodologies need to be formulated.

8. Standardization of laboratory procedures and techniques for interpreting instrumental analysis data (especially LRMS) is essential if data from different laboratories are to be comparable. Thus, analytical information assimilation through IERL-RTP is being emphasized.

Assessing the potential for environmental damage from complex industrial sources is an awesome and formidable task but one which is necessary for providing guidance for pollution control needs, control technology development, health and ecological research, and regulatory/standards-setting activities.

The phased approach to environmental assessment as described in this report is indeed on the right road to fulfilling its primary purpose, namely, to identify in a cost-effective manner the environmental problems associated with industrial processes and fossil energy systems. This methodology is proving especially valuable in predicting potentially adverse effects from emerging technologies, such as coal gasification and liquefaction. In such cases, it is vital to project the likely environmental problems while these processes are still in the pilot or demonstration-scale stages, so that appropriate pollution control measures will be available when the processes are ready for full-scale commercialization.

The IERL-RTP approach to environmental assessment is an iterative and evolutionary methodology, improving as faults are revealed and as new information becomes available. At its present level of development, it provides a valuable framework and focus for environmental assessments.

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THE PERMITTING PROCESS FOR NEW SYNFUELS FACILITIES

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ABSTRACT

The Environmental Protection Agency and the respective State Departments of Health are involved in a joint partnership with shared responsibilities for protecting the environment during the development of synthetic fuels. Legislation in the form of the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, Safe Drinking Water Act, and the Toxic Substances Control Act provide the framework for EPA's regulatory responsibilities. The current status of implementing regulations and agency policies vis-a-vis these Acts is provided in this paper. Also, important aspects of State environmental regulations are provided.

Permit applications for synthetic fuels facilities are being received by EPA Regional Offices and by State agencies. Synfuels EISs are being reviewed. Decisions on Best Available Control Technology are being made. These engineering judgements are also discussed in this paper.

THE PERMITTING PROCESS FOR
NEW SYNFUELS FACILITIES

Table 1 not cited T 3 cited as T-2 in 2nd citation this p.

I. INTRODUCTION

EPA has legislative mandates to protect air and water quality, to insure a safe drinking water supply, and to provide for an environment conducive for the enjoyment of man on this earth. In order to accomplish these goals, EPA is involved in a partnership with State and local agencies in the formulation and enforcement of regulations which implement the legislative intent. A major component of the regulatory process is the requirement for industrial operations such as synthetic fuels facilities to obtain a permit for the project. This paper discusses the EPA permit mechanism and its framework (Table 1).

II. LEGISLATION

The general process of legislation/regulations is that the U.S. Congress establishes environmental legislation that provides a framework for State legislation and implementation of Federal and State regulations. State legislation and regulations can be more (but not less) stringent than Federal requirements if a State is delegated responsibility for administering the program in a given media. The Federal government retains an oversight/reviewing role for those programs that are delegated to the States. State legislation in general parallels Federal legislation in form and substance. The following discussion highlights the major aspects of the legislative mandates of EPA as it applies to a synthetic fuels industry.

Clean Air Act

Under the Clean Air Act (PL 95-95) synthetic fuel facilities must: (a) employ Best Available Control Technology (BACT), (b) insure that National Ambient Air Quality Standards (NAAQS) (Table 2) are not violated, (c) not violate the prevention of significant deterioration (PSD) ambient air quality increments (Table 3) (40 CFR 52.21), (d) not significantly degrade visibility in mandatory Class I areas (40 CFR 51), and (e) perhaps obtain up to 1 year of baseline data before applying for a PSD permit to construct and operate. BACT has been defined in the form of allowable emissions limits and control device operational characteristics. Source monitoring, ambient monitoring, record keeping and reporting requirements are also part of the PSD permit. (40 CFR Part 60.7) Also EPA has the ability to request monitoring data, to take enforcement actions, and to take administrative and judicial actions if there are any emergency episodes of pollutants that present an imminent and substantial endangerment to public health.

T-3

Table 1

Synfuels Permits

Permit Title	Jurisdiction
1. Environmental Impact Statement (EIS)	Federal
2. Resource Recovery and Conservation - definition and control	Federal
3. Toxic Substances-definition and control	Federal
4. National Pollutant Discharge Elimination Systems (NPDES)	Federal
5. Prevention of Significant Air Quality Deterioration	Federal
6. Soil Prevention Control and Countermeasure (SPCC)	Federal
7. Well Operation Permit(underground Injection)	Federal
8. Erection of Towers or Other Tall Structures	Federal
9. River and Stream Crossing Permit	Federal
10. Major Fuel Burning Installation Approval	Federal
11. Rights of Way Across Public Lands	Federal
12. Scientific, Pre-Historic and Archeological	Federal
13. Sundry Notices and Reports on Wells	Federal
14. Oil Shale Mineral Rights Lease	Federal
15. Detailed Development Plan	Federal
16. Collection of Environmental Data and Monitoring Plan	Federal
17. Exploration and Mining Plans	Federal
18. Mine Safety and Health definition and control	Federal
19. Notice of Intent to Prospect	State
20. Permits for Special Operators	State
21. Permit for Limited Impact Operations	State
22. Permit for Regular Mining Operations	State
23. Storage of Flammable Liquids	State
24. Application for Diesel Permit - Underground Operations	State
25. Operator's Notice of Activitiy	State
26. Hoistman Certificate	State
27. Application to Store, Transport and Use Explosives	State
28. Reservoir Construction	State
29. Water Well and Pump Installation (requirements)	State
30. Air Contaminant Emission Notices	State

Table 1 (continued)

Permit Title	Jurisdiction
31. Land Use Special Permit	State
32. Air Contaminant Emission Permit	State
33. Fugitive Dust Permit	State
34. Open Burning Permit	State
35. Subsurface Disposal Permit	State
36. Discharge Permit	State
37. Waste Disposal Plant Operator Certificate	State
38. Potable Water Supply and Safety Compliance	State
39. Sewage Plant Site Approval and Plant Approval	State
40. Purchase, Transportation and Storage of Explosives	State
41. Oil Facility Inspection	State
42. Boiler Inspection Permit	State
43. Oil Shale Leases	State
44. Ground Water Well Application	State
45. Application for Water Rights	State
46. Mined Land Reclamation	State
47. Permit for Exploration and Excavation	State
48. Open Burning	State
49. Fuel Burning-Sulfur Content Exemption	State
50. Permit to Construct Facilities that are Sources of Air Pollution	State
51. Permit to Construct and Operate Treatment Works	State
52. Water Quality-Definition and Control	State
53. Permit to Operate Solid Waste Disposal Site	State
54. Notice of Intention to Operate or Suspend Operations	State
55. Hoistman-Qualifications	State
56. Escape and Evacuation Plans	State
57. Boiler and Pressure Vessel- definition and control	State
58. Storage of Explosives	State
59. Construction of Wastewater Ponds and Holding Facilities	State
60. Construction of Sewage Facility	State
61. Subsurface Discharges	State
62. Mining Permit, Mining and Reclamation Plan	State
63. Notification of Mining Operations(control)	State
64. Discharges-In Situ Mining	State
65. Construction and Operating Permit for New or Modification to Existing Facility	State

Table 1 (continued)

Permit Title	Jurisdiction
66. Open Burning Permit	State
67. Permit to Dispose of Hazardous Wastes	State
68. Approval for Construction and Operation of Waste Facility	State
69. Construction and Operating Permit for New or Modification to Existing Facility	State
70. Exploration Permit, License to Explore	State
71. Industrial Zone Change	County
72. Conditional Permit	County
73. Mineral Extraction	County
74. Rights-of-Way Approvals	County
75. Solid Waste Disposal	County
76. Rezoning Permit	County
77. Temporary Use Permit	County
78. Conditional Use Permit	County
79. Building Permit	County
80. Special Use Permit	County
81. Sewage Disposal	County
82. Solid Waste Disposal Permit	County
83. Conditional Use Permit	County
84. Sewage Disposal System	County
85. Installation of Utilities in Public Right-of-Ways	County
86. Driveway Permit Across County Roads	County
87. Recreation Forest and Mining Zone (RF&M)-definition and control	County
88. Mining and Grazing Zone (M&G-1) definition and control	County
89. County Requirements in Addition to the Mining and Grazing (M&G-1) and Recreation Forest and Mining (RF&M)Zoning Requirements	County

TABLE 2 NATIONAL AMBIENT AIR QUALITY STANDARDS, UG/M^3***

Pollutant	Averaging time	Primary standard	Secondary standard
SO_2	Annual	80	---
	24 hour	365	---
	3 hour	---	1,300
Particulate matter	Annual	75	60
	24 hour	260	150
NO_x (as NO_2)	Annual	100	100
O_3	1 hour	240	240
CO	8 hour	10,000	10,000
	1 hour	40,000	40,000
Lead	Quarterly	1.5	1.5
HC (non CH_4)	3 hour	160***	160***

* 40 CFR Part 50

** Reference conditions = 760 mm Hg and 25°C

*** Not a standard; a guide to show achievement of the O_3 standard

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TABLE 3 PREVENTION OF SIGNIFICANT DETERIORATION OF AIR QUALITY (PSD) STANDARDS*

Pollutant	Averaging time	Maximum Allowable Increase, mg/m^3 Class I	Class II	Class III
Particulate matter	Annual	5	19	37
	24 hour	10	37	75
SO_2	Annual	2	20	40
	24 hour	5	91	182
	3 hour	25	512	700

* 40 CFR 52.21 and 42 USC 7401 et seq section 163.

Notes:

1. Variances to the Class I increments are allowed under certain conditions as specified at Section 165(d)(c)(ii) and (iii) and at 165(d)(D)(i) of the Clean Air Act of 1977.

2. EPA was to have promulgated similar increments for HC, CO, O_3 and NO_x by August 7, 1979; they are under development. Increments for Pb are due to be promulgated by October 5, 1980.

Clean Water Act

The Clean Water Act (PL 95-2]7) established goals of (a) no discharge of pollutants into navigable streams by 1985, (b) attainment by July 1, 1983, of water quality suitable for protection and propagation of fish, shellfish, and wildlife and provides for recreational use, and (c) prohibition of discharges of toxic amounts of toxic pollutants. The Act contains requirements in sections 402 and 404 for potential permits for synthetic fuel facilities. A National Pollutant Discharge Elimination System (NPDES) permit must be obtained under requirements of Section 402 if water is discharged to a navigable stream (defined as waters of the United States and in fact could be a dry creek bed which flows during runoff). Neither effluent guidelines (Section 304) nor New Source Performance Standards (Section 306) have been promulgated for any synthetic fuels operations. However, in their absence, NPDES effluent limits are established on a best engineering basis. A Section 404 permit must be issued by the Army Corps of Engineers and concurred upon by EPA if any dredge and fill operations take place in a navigable stream (defined for 404 purposes as stream flow greater than 3 cfs). Section 303 of the Act provides the mechanism for establishing water quality stream standards. Plans developed by State Water Pollution Control Agencies must define water courses within the State as either effluent-limited or water-quality-limited. Best management practices (BMP's) to control nonpoint source runoff may be defined via section 208 and 304(e) of the Act.

Safe Water Drinking Water Act

Underground injection control (UIC) regulations proposed on April 20, 1979 (Title 40 of the Code of Federal Regulations (CFR), Part 126)were promulgated in the May 19 and June 24, 1980 Federal Register. These regulations will govern the injection or reinjection of any fluids. Permits (40 CFR 122.36) will be required for in situ operations and for mine dewatering reinjection. Various States require reinjection permits under existing regulations. The basic thrust of the UIC program is to require containment of reinjected fluids. Monitoring (40 CFR 146.34) and mitigation measures (40 CFR 122.42) to prevent the endangerment of the groundwater system are requirements under these UIC regulations.

Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) will govern the disposal of solid and hazardous wastes generated by a synthetic fuel facility. Criteria for the identification of hazardous wastes were proposed by EPA on December 18, 1978 at

40 CFR, Part 250. Final regulations were promulgated in the May 19, 1980, Federal Register at 40 CFR 261-265. It appears that some high volume-low risk materials will not be considered a hazardous waste. Instead, it will be subject to requirements at 40 CFR 257 (September 13, 1979, Federal Register). A concept of Best Engineering Judgement will govern the disposal of hazardous wastes such as API separator sludge.

Testing of effects, record keeping, reporting, and conditions for the manufacture and handling of toxic substances are being defined under the auspices of the Toxic Substances Control Act (TSCA) of 1976. An inventory of all commercially-produced chemical compounds is now being compiled and was published in May 1979. If a substance is placed on the inventory, it is "grandfathered" from the TSCA pre-market notification requirements. Ten synthetic fuels were identified on this list of 43,000 compounds. However, these ten are being reviewed to determine the validity of their being placed on the list. Being on the list does not "protect" a product from possible control requirements included in Section 8. If a material is found to be a hazard, certain restrictions including labeling, precautionary handling requirements or even a ban on its production may be imposed by EPA.

The final piece of environmental legislation in which EPA participates which is relevant to synthetic fuels is the National Environmental Policy Act (NEPA). EPA reviews, and in limited cases writes, the EIS when a project involves a major Federal action. EPA's role as a reviewer is to comment on the environmental aspects of the project.

EPA's legislation as described above normally provides a permit process mechanism. Companies wishing to construct and operate a synthetic fuel facility must receive a permit from EPA or from the State permitting authority in order for the facility to be operated. A listing of the major permits/clearances necessary for a project appears in Table 1.

III. APPLICABLE FEDERAL AND STATE POLLUTION CONTROL REGULATIONS

Federal and State legislation generally prescribes the establishment of National and State environmental standards for a given media (i.e. air, water, solid waste, etc.). Regulations designed to control emissions/effluents from an individual facility are promulgated to achieve the stated environmental standards. This section briefly describes this concept of standards/regulations. In almost all cases, the standards/regulations concept requires a developer to obtain a permit to construct and operate his facility. It is the intent of EPA to delegate the permit programs to the State.

Air

Regulations to protect air quality exist in two forms-ambient air quality standards and stack emission standards. All EPA regulations are codified in Title 40 of the Code of Federal Regulations. Applicable parts are referred to in discussions of the various regulations below. Pursuant to Section 109 of the Clean Air Act, EPA has established National Ambient Air Quality Standards (NAAQS) for seven criteria pollutants (40 CFR Oart 50). Primary standards are designed to protect public welfare (vegetation, materials corrosion, aesthetics, etc.). States may also establish ambient air quality standards.

The Clean Air Act also established the concept of prevention of significant deterioration (PSD) of air quality designed to protect clean air areas (40 CFR Part 52.21). Class I areas include national parks larger than 2,428 ha(6,000 acres), national wilderness areas greater than 2,023 ha(5,000 acres), and international parks, and national memorial parks that exceed 2,023 ha (5,000 acres). Areas in the United States that presently have lower ambient air quality than that specified in the NAAQS are designated as nonattainment areas; the remainder of the United States is designated Class II. Redesignation of Class II areas to either Class I or Class III by the state is possible. Recent court rulings have resulted in some major changes in the PSD regulations which appear in the August 7, 1980 Federal Register.

A second ambient air quality consideration is the visibility protection afforded to Federal Mandatory Class I areas via Section 169A of the Clean Air Act (40 CFR, Part 51). Regulations are to be promulgated by EPA (November 1980) and the States (August 1981) that are designed to prevent visibility impairment in the Federal Mandatory Class I areas. Since there are many issues to be resolved, it is too early to delineate the potential implications of the visibility regulations. Proposed regulations appeared in the May 22, 1980, Federal Register at 40 CFR 51.300. An EPA Report to Congress on visibility was published in November 1979.

Limitations on the amounts of pollutants emitted from a synthetic fuel facility are the enforceable mechanism to assure that the NAAQS and PSD increments are not violated. EPA establishes New Source Performance Standards (NSPS) 40 CFR Part 60), States establish emission standards, and EPA (or the State) must define emission limits that reflect the BACT. NSPS have not been defined for synfuels facilities, but BACT has been defined for five oil shale facilities and one coal gasification via the PSD permit process.

Water

Water pollution control requirements exist in the form of Water Quality Criteria, State Water Quality Standards, Drinking Water Standards, National Pollutant NPDES limits, and effluent guidelines. The following discussion summarizes the major aspects of surface water and groundwater quality standards; a complete discussion of the enforceable mechanism to attain these standards, that is the NPDES and UIC permit systems, may be found in other EPA references. (1)

Surface Water Quality Standards

Water quality standards are addressed in Section 303 (Water Quality Standards and Implementation Plans) of the Clean Water Act. Excerpts and summaries of requirements for establishment and implementation of water quality standards of that section are presented below:

Water quality standards shall be reviewed at least every 3 years by the Governor or State Water Pollution Control Agency and shall be made available to the Administrator.

State revised or adopted new standards shall be submitted to the Administrator (EPA) for approval. Such revised or new water quality standards shall consist of the designated uses of the navigable waters involved and the water quality criteria for such waters based upon such uses. Such standards shall be such as to protect the public health or welfare, enhance the quality of water, and serve the purposes of the Act(FWPCA). Such standards shall be established, taking into consideration their existing or intended potential use and value for public water supplies, propagation of fish and wildlife, recreational purposes, agricultural, industrial, and other purposes, while also taking into consideration their use and value for navigation.

Each State shall identify those waters for which existing or proposed effluent limitations are not stringent enough to attain established water quality standards and establish waste load allocations for those waters. Regulations promulgated at 40 CFR 131.11 and further discussed in the December 28, 1978 Federal Register describe the Total Maximum Daily Load concept.

Each State shall identify those waters or parts thereof within its boundaries for which controls on thermal discharges are not sufficiently stringent to assure protection and propagation of a balanced indigenous population of shellfish. fish, and wildlife.

(1) Environmental Perspective on the Emerging Oil Shale Industry, November, 1980.

The 208 Process

Section 208 of the FWPCA required States to designate areawide waste treatment planning agencies. These 208 agencies are to plan, promulgate, and implement a program designed to protect surface water quality. Stream classifications and water quality standards are to be developed.

Local input in most States on the proposed stream use indicated a desire to assign multiple classification systems wherever possible. Although the apparent intent of State classification systems (1978) is simply to identify the criteria applicable to a given stream segment, there is considerable local concern that a single "use" classification may be used later to restrict other uses, particularly agricultural ones. Intermittent streams have not been classified because of provisions made for this situation in the proposed classification system.

As an example, the four combinations of multiple use classifications that are proposed for Colorado include:

Class 1: Aquatic Life. Water Supply, Recreation, and Agriculture
Class 2: Water Supply, Recreation, and Agriculture
Class 3: Recreation and Agriculture
Class 4: Agriculture

The proposed water quality standards allow exceptions under certain conditions. Using the guidelines in the proposed criteria, the water quality data base, the proposed water quality criteria, the existing water quality problems, and a subjective analysis of potential effectiveness of potential control measures, three types of exceptions were identified for Colorado:

- Permanent exception - The current criterion limit is not valid for the drainage area because of natural environmental conditions. It is assumed that, given a return to prehistoric conditions, this parameter would still violate the criterion limit. The parameter should be monitored regularly, and any trend of increasing concentration would require evaluation/investigation of possible causes beyond natural conditions. It is further assumed that it is uneconomical to attempt controlling runoff.

- Temporary exception (10 Years) - This exception is requested when a criterion violation is identified as a possible consequence of man's activities in the basin and management strategies are available to improve water quality, but it will take 19 years to evaluate effectiveness.

- Temporary Exception (5 Years) - This exception is requested when a limited data base indicates a problem but more data are required to identify the cause, extent, and correctability of the problem. The 5-year exception should allow sufficient time for necessary additional data collection and analysis.

Ground Water Quality Standards

Federal - Federal regulations that may pertain to groundwaters are addressed in the Safe Drinking Water Act. This act has most recently been interpreted as applying to well injection of waste into aquifers that do or that might serve as sources for public drinking water. Such underground drinking water sources, while specified to include aquifers with less than 10,000 mg/l total dissolved solids, must have the potential to be sources of public water supply. Underground injection control (UIC) regulations were promulgated at 40 CFR 126 on May 19, 1980. In situ operations will fall into the category of "Class III wells". Drinking water standards are listed in Tables 4 and 5. Note that pits, ponds, and lagoons are not identified as underground injection sources at this time. They are covered under the RCRA.

Solid and Hazardous Wastes

The RCRA requires that solid and hazardous waste generators and transporters receive permits and that wastes be disposed only by safe practices. Regulations have been promulgated at 40 CFR Part 261 for (1) the criteria to identify solid and hazardous wastes (Section 3001); (2) disposal standards (Section 3004); and (3) permit programs (Section 3005). If a waste is not defined as hazardous (i.e., it is defined only as a solid waste) disposal will be governed by the Section 4004 regulations as promulgated at 40 CFR Part 257 on September 18, 1979. The promulgated regulations defined a waste as hazardous if it is ignitable (flash point $<$ 60° C or 140° F), corrosive (extract pH $\leq$ 2 or $>$ 12.5), reactive (explosive or oxidizing) , or toxic (extract concentration is 100 times greater than drinking water standards). Over burden mine wastes that are returned to the mine are exempt from these regulations. Also, materials ready for further processing are exempt.

RCRA regulations probably will result in materials such as API separator sludge, spent catalysts, gasifier ash, distillation tank bottoms and perhaps others being defined as a hazardous waste.

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TABLE 4 PROMULGATED DRINKING WATER STANDARDS (40 CFR 141)

The following are the maximum contaminant levels for inorganic chemicals other than fluoride:

Contaminant	Level, mg/l
Arsenic	0.05
Barium	1.
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10.
Selenium	0.01
Silver	0.05

When the average of the maximum daily air temperatures for the location in which the community water system is situated is the following, the maximum contaminant levels for fluoride are:

Temperature, °F	°C	Level, mg/l
53.7 and below	12.0 and below	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

The following are the maximum contaminant levels for organic chemicals. They apply only to community water systems. Compliance with maximum contaminant levels for organic chemicals is calculated pursuant to Section 141.24.

	Level, mg/l
a. Chlorinated hydrocarbons:	
Endrin (1,2,3,4,10, 10-hexachloro-6.7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1.4-endo-5,8-dimenthano naphthalene).	0.00002
Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer).	0.004
Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl) ethane).	0.1
Toxaphene ($C_{10}H_{10}Cl_8$-Technical chlorinated camphene. 67-69 percent chlorine).	0.005
b. Chlorophenoxys:	
2,4-D, (2,4-Dichlorophenoxyacetic acid).	0.1
2,4,5-TP Silvex (2,4,5-Trichlorophenoxypropionic acid).	0.01

TABLE 5 LEVELS OF CONTROL APPLICABLE TO EXISTING SOURCES UNDER 1977 AMENDMENTS TO FWPCA

Pollutant	Conventional	Nonconventional	Toxic		
Name	Best Conventional Pollutant Control Technology	Best Available Technology Economically Achievable	Best Available Technology Economically Achievable	Effluent Standards (or Prohibitions)	Best Management Practices
Abbreviation	BCT	BAT	BAT		BMP's
Statutory Deadline	July 1, 1984	July 1, 1984/as appropriate.[a] Never later than July 1, 1987	July 1, 1984/as appropriate[b]	Up to one year after promulgation/ as appropriate[c]	None
301(c) Economic Variance	No	Yes	No	No	No
301 (g) Environmental Variance	No	Yes	No	No	No

[a] July 1, 1984, or three years after limitations are established, whichever is later. Never later than July 1, 1987.

[b] July 1, 1984 for those 129 toxic pollutants which appeared at 43 Federal Register 4108 (January 30, 1978). For other pollutants which may be added to the toxics list, three years after limitations for such pollutants are established.

[c] The effective date for an effluent standard for a toxic pollutant may be extended to three years after the standard is promulgated if earlier compliance is technically infeasible.

IV. PROPOSED PRECOMMERCIAL APPROACH TO INDUSTRY STANDARDS

The approach regulating the first synfuels facilities must ensure compliance with existing standards, but, more important, should emphasize characterization of residuals from the facility. EPA Region VIII has expressed their desire to see a synfuels industry proceed in a phased orderly manner. Rigorous testing programs and data analyses should be performed on the first facilities, which would be representative of commercial size. Comprehensive monitoring of emissions, effluents, and waste materials should be performed. Research programs designed to define the optimum control technology for a given pollutant for a synfuels industry should be conducted. Trade-offs among air pollution, water pollution, and solid waste must be defined. The energy penalty, water consumption, and cost of control must be defined. The comprehensive monitoring efforts should not be limited to only the regulated pollutants, but should characterize nonregulated pollutants.

As previously stated, emphasis should be placed on source characterization. A moderate degree of ambient impact monitoring should be performed to validate predicted impacts and to document trends and changes from baseline. Programs to evaluate effects on receptors should be performed to provide feedback on the source and ambient monitoring programs. There are two principal bases for writing permits for synfuels facilities. The first relies upon the transfer of pollution control technology from related industries. The second relies upon the development of EPA's Pollution Control Guidance Documents.

The BACT for air pollutants must be employed for any proposed synfuels facility with the potential for emitting 91 tonnes (100 tons) or more (controlled) per year of any regulated air pollutant. Those facilities that have smaller potential emissions do not need BACT but should perform comprehensive monitoring in order to develop emissions data for potential permit applications. Two primary mechanisms exist to define the BACT. First, several synfuels facilities have received Prevention of Significant Deterioration (PSD) permits. The BACT has been defined on a case-by-case basis for these facilities. Second, air pollution control technology that has been defined as the BACT for synfuels related facilities may be considered as transferable to the industry. It is highly likely that air quality requirements may prove to be the governing constraing to the size of synfuels industry in certain parts of the country. Therefore, in order to maximize the amount of oil production capability of oil shale country it is important to maximize the air emissions control for each facility.

A no-discharge-of-pollutant concept is being considered by several developers as a means of handling their wastewater streams. Three types of water should be considered--mine, process, and in situ water. A no-discharge-of-process-water concept has been written into water permits. If any water is discharged to surface streams or reinjected into the groundwater system, it would consist of mine inflow (but not process or in situ water) or uncontaminated surface runoff. Treatment may or may not be necessary. Effluent limitations will be defined for certain pollutants including toxics for certain process streams in the NPDES permit. Best available technology economically available (BATEA) must be provided. (See Table 6). Major concepts to be addressed by regulatory agencies and the developer are summarized as follows. First, because of the semi-arid, water-short condition of potential development areas, it may be environmentally best to encourage treatment if necessary and discharge to a surface stream of mine water. Second, because of salinity considerations, treatment of mine water and/or minimization of water consumption is a desirable policy. Third, disposal of process water onto processed shale piles or ash piles without treatment may not be desirable. The high organic and salt concentration of the process water may represent too great a risk to groundwater/surface water quality because of potential catastrophic events or unexpected permeabilities/leaching., and they represent a deterrent to successful revegetation. Fourth, maximum recycling and reuse of process and nonprocess water will be encouraged; cost effectiveness must be considered. Finally, land application of untreated mine water may be desirable only for a short period of time because of the potential nonpoint source runoff problems.

Solid and hazardous wastes should be disposed of in a manner that avoids contact with water and subsequent toxic concentrations. Disposal practices should also be designed that preclude (or at least minimize) the potential for the solid material from becoming airborne as a fugitive dust. Safe disposal practices as defined at 40 CFR 264 apply to synfuels facility hazardous wastes such as spent catalyst, API separator sludge, tank bottoms, cooling tower sludge, and water treatment plant sludge. Surface disposal for solid wastes from a synfuels industry at a minimum should conform to those practices found in 40 CFR 257.

Pollution Control Guidance Documents

Regulating new, presently non-existent energy industries, of course, presents different problems from regulating long-standing segments of United States industry. The differences are of such an extent that a unique regulatory approach is demanded. The differences arise primarily from the facts that the new energy industries are, for the most part, not yet

TABLE 6. NEW SOURCE PERFORMANCE STANDARDS FOR SYNFUELS RELATED ACTIVITIES

40 CFR 60.40 Subpart D (NSPS for Fossil Fuel Fired Steam Generators)	
TSP	0.10 pound per million BTU
SO_2	0.80 pound per million BTU (liquid fuel)
NO_x	0.20 pound per million BTU (gaseous fuel) 0.30 pound per million BTU (liquid fuel)
40 CFR 60.100 Subpart (NSPS for petroleum refineries)	
H_2S	0.10 grain/dscf
HC	Floating roof or vapor recovery if true vapor pressure is >1.5 psia but < 11.1 psia reporting requirements only if true vapor pressure is < 1.5 psia.
40 CFR 60 (NSPS for Refinery Claus Sulfur Recovery Plants)	
Gaseous fuel burning	0.1 grain/dscf
Sulfur recovery	
oxidation system	250 ppm SO_2
reduction system	300 ppm total S 10 ppm H_2S
Proposed NSPS	
1. Gas Turbines >10 x 10^6 BTU/hour	
	75 ppmv NO_x at 15% O_2 150 ppmv SO_2
2. Coal Gasification (Guideline)	
	250 ppmv total S 99.0 percent total S removal 100 ppmv HC
3. Field gas processing units	
Gaseous fuel burning	160 ppmv H_2S
Sulfur recovery	250 ppmv SO_2 (oxidation) 300 ppmv S (reduction)

commercialized in the United States and have potentially different effluents and emissions from those from existing pollution sources.

There is , unfortunately, little or no existing source of commercial-scale data on which to base a "conventional" regulatory approach at this time. In some instances standards from related industries may be borrowed. (See Table 6) Because of these circumstances, the general approach we are taking is to issue, as pre-regulatory guidance, a series of Pollution Control Guidance Documents, PCGD's -- one for each of the major energy technologies. The focal point of each PCGD is to be a set of recommendations on available control alternatives for each environmental discharge along with associated performance expectations. The basis for these recommendations will be presented. The intent is to present guidance for plants of typical size and for each significantly different feedstock likely to be used. PCGD's will not have the legally binding authority of regulations but each will be reviewed extensively both within and outside of EPA. These documents will provide useful and realistic guidance to permit writers within EPA and the States and to the energy industry itself during its formative stages. As the energy industry develops, permits for individual installations are being issued based on best engineering judgment and, as the various PCGD's become available, permits will be prepared in light of the information the PCGD's contain. Then, as the energy technologies mature, EPA will invoke its normal regulatory procedures: in the water quality area, for example, the issuance of effluent guidelines and establishment of appropriate water quality standards.

It is clear that for most new energy technologies, exemplary full-scale and even pilot-scale waste treatment installations do not yet exist. Moreover, there is a unique chance not available to actually influence, in an environmentally productive way, the choice by industry of the very process technology to be commercialized and the overall designs of new plants such that the most cost-effective environmental protection methods can be incorporated into process design from the very beginning so that more expensive pollution control retrofitting is minimized or eliminated. The Pollution Control Guidance Documents, therefore, have two key purposes: (1) to aid permit writers in preparing realistic, comprehensive permits for the energy industry by describing and characterizing projected waste discharges from the various energy technologies under development and by providing the best possible information on the expected cost and performance of the variety of control options that appear applicable and (2) to provide guidance to the energy industry itself with regard to the kinds of environmental impacts with which EPA will be concerned for their particular kind of facility, the control options which EPA has deemed to be potentially applicable and EPA's projections of probable cost and performance of the various options.

Let me now elaborate on the general structure of PCGD's. The Document will consist of three Volumes. Volume I is a summary report including recommended pollution control technology options and related costs; Volume II is a detailed report describing pollutants, waste streams and alternative control options, including cost and performance; Volume III is an appendix providing the data base for stream and pollutant characterization and control costs and performance.

The major users of the PCGD's are expected to be the permit writers. The Document for a particular energy technology should help them to better understand permit applications and to prepare a proper permit. Best available control technology will be suggested but information on alternative control methods will also be provided for use in considering site-specific situations. For example, a permit writer may be faced with having a very small allowable incremental increase in an air pollutant, say sulfur dioxide, when conducting a Prevention of Significant Deterioration (PSD) review. The PCGD will, hopefully, let him consider alternatives that achieve stringent control but will also indicate what the cost of such a level of protection would be.

The Documents will also serve as a beginning for future data base developers and regulation writers. When the industry becomes commercialized, the EPA program offices responsible for preparing regulations will need to collect commercial-scale data as the basis for authoritative regulations. The data base in the PCGD's should serve as a guide to identifying needs, organizing and carrying out these future data collection efforts.

For the developers, the PCGD's should influence the choices they have to make on control options and even on certain process alternatives. If industry and the other Federal and State agencies which directly support energy development are aware of anticipated environmental problems and available control technologies, their development and plant design efforts can incorporate features which will help to avoid the necessity for future retrofitting of control technology.

It shoud be noted that providing an early indication of EPA's concerns for various pollutants and options on pollution limits will not just produce "passive reactions". On whatever information EPA provided, it will receive feedback and criticism. By precipitating this feedback process while the energy technologies are still being developed, many issues regarding environmental protection should be resolved prior to construction and operation. The advance notice of EPA's thinking will permit regulators, developers and other segments of the public to work together to a greater degree than has been possible in the past and should result in the development and commercialization of an environmentally sound energy industry.

The specific energy technologies for which separate PCGD's are now planned are the following:

- Low Btu Coal Gasification
- Indirect Coal Liquefaction
- Oil Shale (mining and milling)
- Direct Coal Liquefaction
- Geothermal (first revision of existing PCGD)
- Medium Btu Coal Gasification
- High Btu Coal Gasification

Table 8 provides the schedule for their development.

EPA has taken specific measures to assure that the development of regulatory approaches for the energy industries will involve a wide range of interested parties, both in the preparation of PCGD's and in their review. These parties include government, industry, environmentalists and the public in general. Within EPA, we have established an Alternate Fuels group which has the responsibility for coordinating all research and all regulation development--on a multi-media basis--for new energy technologies. Serving on this group are representtatives from all of the major policy/program and research offices charged with related research and regulation development and from some of the Regional Offices which are most concerned with synfuels commercialization. The Group's overall responsibility is to develop the EPA regulatory approach for the new energy technologies. Within this context the Alternate Fuels Group is charged with producing Pollution Control Guidance Documents, overseeing the creation of a program to insure the development of coordinated standards taking into account cross-media pollutional impacts and generating and updating a research plan. Under the Alternate Fuels Group are various "work groups" which concentrate on specific energy areas. There are separate work groups for oil shale mining and retorting, coal gasification, indirect coal liquefaction , direct coal liquefaction, alcohol production and geothermal energy. The members of the work groups are EPA employees but we have also invited participation from other involved Federal agencies, viz., the Department of Energy (DOE), the Tennessee Valley Authority (TVA) and the Department of the Interior (DOI).

The Pollution Control Guidance Documents will go through an extensive internal and external review process. Internally, the Alternate Fuels Group and the relevant work group will be directly involved but final sign-off will occur at the level of the Agency's Assistand Administrators who serve on EPA's Energy Policy Committee, the Agency's highest level energy coordination group. Externally, the Documents will be reviewed

TABLE 7. POLLUTION CONTROL GUIDANCE DOCUMENT REVIEW SCHEDULE

Technology	1st Draft (data base)	Public Forum	Final Publication
Low Btu Gasification	11/80	4/81	8/81
Indirect Liquefaction	11/80	5/81	9/81
Oil Shale	11/80	5/81	9/81
Direct Liquefaction	9/81	3/82	7/82
High Btu Gasification	4/82	10/82	2/83
Medium Btu Gasification	1/82	7/82	11/82

Table 8 Processes To Be Covered In Pollution Control Guidance Documents Now Under Preparation

o Low Btu Gasification
(Single State, Atmospheric Fixed Bed)

- Riley-Morgan
- Wilputte-Chapman
- Wellman-Galusha

o Indirect Coal Liquefaction

Gasification	Synthesis
- Texaco	Coal-To-Methanol
- Lurgi	Mobil "M" (Methanol for Gasoline)
- Koppers Totzek	Fischer-Tropsch

o Oil Shale

- TOSCO II
- Paraho
- Union
- Superior
- Occidental
- Rio Blanco

o Direct Coal Liquefaction

- H Coal
- SRC
- Exxon Donor Solvent

by other Federal organizations such as DOE, TVA and DOI and by a wide variety of industrial reviewers and also public interest groups. Associations such as the American Gas Association, the Gas Research Institute and the National Council of Synfuels Producers will also serve as reviewers. A public forum providing a second opportunity for external review will be announced in the Federal Register sixty days prior to its occurrence. Review comments from individuals and from technical societies such as the Federation will be most welcome. The final Document will be revised to reflect response to all appropriate comments. The proposed review schedule for the six PCGD's now under preparation or planned is shown in Table 1.

Although the major objective of a PCGD is to recommend pollution control options, it will contain a great deal of background information on the energy processes themselves and on process streams and pollutant concentrations, and will, on the basis of a series of "case studies", offer specific technology based control guidance for various kinds of energy processes. Processes to be included will cover those that are expected to be built for demonstration or commercial application first. Table 9 shows planned process coverage for the four PCGD's currently being written). It is intended that discussion of product (E.G., liquefied coal) uses also will be included if use is integral with the manufacturing process. The process descriptions will detail the key features of each process and their pollution potential. If various process modifications are likely to be used at different locations, the changes in process configuration will be covered and expected changes in pollutant releases will be indicated. Pollutant releases that vary non-linearly with plant size or flow rates will also be identified and quantified to the extent possible.

The environmental control alternatives to be considered will include both end-of-pipe treatment techniques and process changes. Candidate control alternatives will be identified from existing United States and foreign bench-pilot-and commercial-scale facilities or from different United States or foreign processes that have similar discharges. Performance and design will be included as will information on capital, operating and annualized costs. Energy usage for control alternatives will also be included. Finally, techniques for monitoring control performance will be identified. The source of all data will be clearly referenced to allow referral to original sources; uncertainties in the data will be indicated.

V. CONCLUSION

Permits to construct and operate synthetic fuel facilities must be obtained by developers. The basis for review of these permit applications is contained in various EPA regulations, standards, and guidance documents. EPA and the respective State agencies have a shared responsibility in the review, permitting, and ensuring compliance of synfuels facilities.

THE TVA AMMONIA FROM COAL PROJECT

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TVA's Ammonia from Coal Project involves retrofitting a coal gasification process to the front end of its existing 225-ton-per-day ammonia plant. The purpose of the project is to develop design and operating data to assess the technological, economic, and environmental aspects of substituting coal for natural gas in the manufacture of ammonia. Preliminary operation of the facility was begun in September 1980. In the absence of specific environmental guidelines for coal gasification processes, TVA's approach to the potential environmental problem is to meet or exceed the emission control requirements for specific components, i.e., sulfur compounds, particulates, aqueous discharges, etc. Also, TVA's facility contract specified limits on certain discharges based on anticipated guidelines. In addition to a discussion of the emissions control activities, a program is described that examines the environmental health and safety aspects of the Ammonia from Coal Project.

THE TVA AMMONIA FROM COAL PROJECT

TVA's Ammonia from Coal Project involves retrofitting a coal gasification process to the front end of its existing 225-ton-per-day ammonia plant. The purpose of the project is to develop design and operating data to assess the technological, economic, and environmental aspects of substituting coal for natural gas in the manufacture of ammonia. Preliminary operation of the facility began in September 1980.

The environmental considerations for this project were unique; no environmental regulations presently exist specifically for coal gasification facilities. TVA's approach to the problem was to meet or exceed the emission control requirements for specific components, i.e., sulfur compounds, particulates, aqueous discharges, etc. In addition, TVA's facility contract specified limits on certain discharges based on anticipated guidelines.

The facility is designed to produce 60 percent of the feed gas required for the 225-ton-per-day ammonia plant. The ammonia plant can operate at 60 percent turndown, therefore, the ammonia plant can operate at its design rate with 60 percent of the feed gas supplied from coal and the remaining 40 percent from natural gas; or, the plant can be operated at 60 percent of design rate (135 tons per day of ammonia) with all the feed gas supplied from coal. The capability of operating the ammonia plant with 100 percent natural gas feed is retained. This arrangement will make the greatest use of the existing ammonia plant and minimize the amount and size of new equipment required. Also, the coal gasification facilities can be operated independently from the ammonia plant by burning the carbon monoxide and hydrogen gas in an existing steam boiler.

The coal gasification unit is based on the Texaco partial oxidation process. Engineering, procurement, and erection of the coal gasification and gas purification facility was done by Brown and Root Development, Inc. The air separation plant required to provide high purity oxygen and nitrogen for the process was handled similarly by Air Products and Chemicals, Inc. Engineering, procurement, and construction of the coal handling and preparation area, interconnections to the existing ammonia plant, slag disposal, and services and utilities required for the complex were performed by TVA.

A flow scheme for the TVA Ammonia from Coal Project (ACP) is shown in Figure 1. Coal is received by rail and is sent to open storage and later recovered by front-end loader or it is crushed in a primary crusher to minus 1/2-inch and conveyed directly to the coal slurry preparation area.

Coal is pulverized in disk mills as required for the gasifier operation. Water is added to the disk mills to form a coal-water slurry. From the disk mills, the slurry goes to one of two mix tanks where the solids content of the slurry is adjusted to the desired level. The slurry is pumped to a feed tank and then metered to the reactor at the process rate of about 8 tons of coal per hour. Gaseous oxygen from the air separation plant is fed to the reactor at about 8 tons per hour through a metering system interlocked with the coal slurry feed.

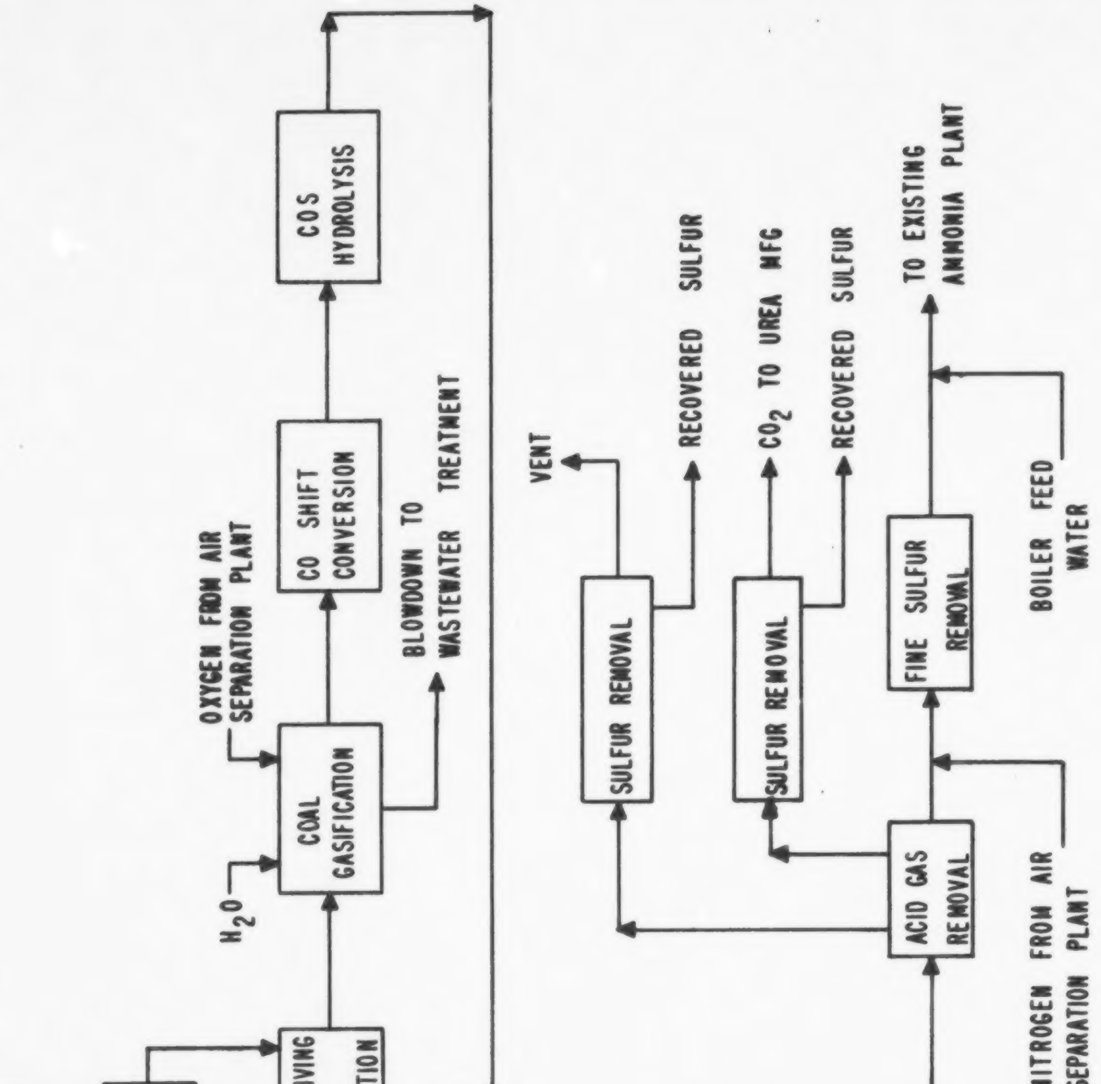
VENT
DUST COLLECTION
COAL RECEIVING AND PREPARATION
H_2O
COAL GASIFICATION
OXYGEN FROM AIR SEPARATION PLANT
BLOWDOWN TO WASTEWATER TREATMENT
CO SHIFT CONVERSION
COS HYDROLYSIS
ACID GAS REMOVAL
NITROGEN FROM AIR SEPARATION PLANT
SULFUR REMOVAL
VENT
RECOVERED SULFUR
SULFUR REMOVAL
CO_2 TO UREA MFG
RECOVERED SULFUR
FINE SULFUR REMOVAL
BOILER FEED WATER
TO EXISTING AMMONIA PLANT

Figure 1 Flow scheme for TVA's Ammonia from Coal Project

The gasification process takes place in the reactor at a pressure of about 510 psig and at a temperature in excess of 2200°F. The carbon in the coal is reacted with steam to produce carbon monoxide and hydrogen. Oxygen is injected to burn part of the coal to provide heat for the endothermic reaction. In addition to the gasification reaction, coal combustion forms carbon dioxide (CO_2), and sulfur compounds in the coal are gasified in the reducing atmosphere to produce primarily hydrogen sulfide (H_2S) and some carbonyl sulfide (COS). Small quantities of other compounds such as ammonia and methane also are formed. According to Texaco's pilot-plant experience, essentially no long-chain or aromatic hydrocarbons are formed.

Slag produced from the ash in the coal is removed from the reactor through a lockhopper system. The slag is glassy in appearance and is very similar to the bottom ash produced in a coal-fired power plant boiler. Initially, trucks are used to transport the solids to a disposal area. A slurry pumping system may be installed later to handle and transport the slag to the disposal area. In such a system, the slag would be washed and screened to remove oversize material which would be crushed to a size suitable for slurrying and pumping.

The gas leaving the reactor is water-quenched and particulate matter (fly ash) is removed in a scrubber. A blowdown to control dissolved solids is taken from the water recirculating loop and pumped to a wastewater treatment facility, which uses chemical, physical, and biological treatment processes. The wastewater is first treated in a clarifier by addition of ferrous sulfate and hydrated lime. The clarifier underflow is sent to a sludge conditioning unit and then to a filter press for solids removal.

The liquid fraction from the clarifier is steam-stripped to remove ammonia which is recovered and routed to the coal slurry preparation area to neutralize the acidic slurry. The stripped aqueous material containing some organic matter, primarily as formates and cyanates, along with water from washdown operations is sent to an equalization-cooling basin for pH control, mixing, and cooling. After aeration, the combined waste then flows to the activated sludge unit for biological treatment. The treated water from the unit is metered and sampled on its way to discharge. The digested sludge flows to the filter press where the solids are removed for disposal. Plans are to recycle the solids to the gasifier. The filtrate is returned to the wastewater treatment system.

The process gas from the quench scrubber flows to two carbon monoxide (CO) shift converters. The converters are charged with a sulfur-activated catalyst marketed by Haldor Topsoe. The design CO content of the gas entering the converter is about 22 percent (wet basis). After full shift, the CO content is about 2 percent which matches the CO content of the gas entering the low-temperature shift converter in the existing ammonia plant.

The COS produced during the gasification process is not affected by the Holmes-Stretford sulfur recovery system that is used to recover H_2S from the off-gas streams from the acid gas removal system. Therefore, the quantity of COS must be decreased to meet the sulfur emission limitations. To accomplish this, a

COS hydrolysis unit containing a catalyst also marketed by Haldor Topsoe is provided between the CO converter and the acid gas removal (AGR) system to promote the reaction:

$$COS + H_2O \rightleftarrows CO_2 + H_2S$$

The process gas from the COS hydrolysis unit flows to the AGR system. The AGR system uses Allied Chemical's Selexol process (a physical absorbent system) to remove the CO_2, H_2S, and the remaining COS from the process gas. This system is capable of decreasing the total sulfur in the synthesis gas stream to less than 1 ppm.

Nitrogen from the air separation plant is added to the process gas from the AGR system to produce an $H_2:N_2$ ratio of 3:1. The gas then flows through a zinc oxide bed to decrease the sulfur content to less than 0.1 ppm. Deaerated boiler feedwater is added to bring the steam-to-dry-gas ratio to 0.44:1. The gas is then heated to about $600^{\circ}F$ prior to its entry into the existing ammonia plant at a point immediately upstream of the low-temperature CO shift converter. The pressure of the gas at the battery limits is about 385 psig. The composition of the process gas is very nearly the same as the composition of the gas leaving the high-temperature CO shift converter in the ammonia plant. The approximate composition of the gas is shown in Table 1. It should be noted that the Selexol system is capable of decreasing the CO_2 to a value much lower than that shown in the table. The 10.8 percent CO_2 (wet basis) is a design requirement and is not set by Selexol process limitations.

Two reject acid gas streams are produced during regeneration of the Selexol AGR solvent. One stream containing up to 4 percent H_2S is sent to one train in the Holmes-Stretford sulfur-recovery system. The Holmes-Stretford system, furnished by Peabody Process Systems, Inc., uses a proprietary solution containing an oxidized form of vanadium salts. The H_2S is oxidized in the solution to produce elemental sulfur according to the following reaction:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$

As stated before, the COS is unaffected by the Holmes-Stretford system. The reduced metal salt is regenerated by blowing air through the solution. This operation also floats the elemental sulfur to the surface. The sulfur is skimmed off and filtered to produce a wet cake. The tail gas from the Holmes-Stretford system contains about 160 ppmv H_2S, less than 30 ppmv COS, and less than 500 ppmv CO. This stream is vented to the atmosphere under conditions of our emissions permit.

The second stream from the AGR solution regeneration system is relatively pure CO_2. This gas is sent to the second train in the Holmes-Stretford unit and then to a vessel containing zinc oxide to decrease the total sulfur content to less than 0.5 ppm to meet requirements for urea manufacture. This gas will be vented to the atmosphere when the urea plant is not operating.

ENVIRONMENTAL CONSIDERATIONS

The Ammonia from Coal Project management brought TVA's environmental and medical expertise into the project at the very beginning. They worked with

Table 1 APPROXIMATE COMPOSITION OF GAS MANUFACTURED FROM COAL AT THE TVA AMMONIA FROM COAL PROJECT

COMPONENT	PERCENT BY VOLUME	
	WET BASIS	DRY BASIS
HYDROGEN	42.0	60.6
NITROGEN	14.1	20.3
CARBON MONOXIDE[a]	2.3[a]	3.3[a]
CARBON DIOXIDE	10.8	15.6
METHANE	0.1	0.1
ARGON	0.1	0.1
WATER	30.6	
TOTAL	100.0	100.0

BASIS: TOTAL SULFUR = 0.1 ppmv MAXIMUM

STEAM-GAS RATIO = 0.44

HYDROGEN-NITROGEN RATIO = 3.0

NOTE: [a] THE CARBON MONOXIDE CONTENT OF THE GAS IS BASED ON END-OF-RUN CONDITIONS FOR THE SHIFT CONVERSION CATALYST.

the project management team to develop the project specification covering the environmental, health, and safety requirements. These specifications were then included in the contract for the coal gasification project.

An environmental evaluation was made on the project and it was determined that an environmental impact statement was not required. Also, because of its size--180 tons-per-day coal feed rate--and because the plant is scheduled to operate one-half of the available operating time, it was determined that the emissions were sufficiently low so that the plant was not considered to be a major pollution source according to EPA's Prevention of Significant Deterioration (PSD) rules. These two facts shortened considerably the lead time required to obtain the necessary environmental permits. Three State of Alabama permits covering emission to the atmosphere were obtained. One covers the coal receiving, unloading, conveying, and storage. Dust suppression equipment is required at all transfer points as a condition of the permit. A second permit covers the primary coal crushing operation and conveying to the pulverizing and slurrying operation in the gasification section. This permit requires dust suppression equipment at all transfer points and a wet scrubber on the crusher operation. The third permit covers the coal gasification and gas purification unit. This permit restricts the quantity of total sulfur compounds, CO, and NOx compounds that can be emitted to the atmosphere. In addition, an uncontrolled vent is allowed for startup and emergency but its use is limited to a certain number of hours per year; combustion of the vent gases is required.

Wastewater is processed routinely as stated earlier by chemical precipitation, stripping to remove ammonia, biological treatment, clarification, solids separation, pH treatment and finally discharge through a flow and pH monitoring system into an existing NPDES-permitted stream. Our efforts to meet regulations required that we obtain a modification to the existing NPDES permit.

Solid wastes are to be disposed of in a landfill. Because we had no concrete data proving otherwise, and as a precautionary measure considering the developmental nature of the project, TVA elected to handle the slag from the gasification operations as if it were hazardous and accordingly applied to the State of Alabama for permission to dispose of the slag in a nearby site. We lined the disposal pond with a minimum of 2 feet of clay having a permeability of 10^{-7} cm/sec or less. We will accumulate the water drainage from the slag and return it to the gasifier operation. Four monitoring wells, one upstream and three downstream of the disposal pond, are provided for sampling to detect any changes in the groundwater composition.

Environmental Studies

Thus far we have discussed the environmental effort in regard to meeting the applicable regulations and emission standards. In addition to these activities, a program is planned that looks further into the environmental, health, and safety aspects of the ACP. Table 2 lists the study areas, the sources of the samples to be analyzed in evaluating these study areas, and the analyses to be performed on the samples. These analyses will help to evaluate the environmental impact of our project and also may serve as a guide in evaluating the impact of future gasification projects. For instance, we fully expect that the slag studies will show that the slag is nonhazardous and should be handled similarly to the bottom ash from a coal-fired power plant.

Table 2 ENVIRONMENTAL STUDY PROGRAM OUTLINE

STUDY AREA	SAMPLE SOURCE	ANALYSES PERFORMED
Gaseous Emissions Monitoring and Characterization	Sulfur recovery tail gas	Sulfur species Nitrogen species Hydrocarbons Particulates Trace Elements
Liquid Effluent Monitoring and Characterization	Treated effluent Accumulator discharge to wastewater treatment	Priority pollutants (129) Trace Elements Other[a]
Solid Waste Monitoring and Characterization	Gasifier slag Solids to landfill (from wastewater treatment) Background Monitoring wells	Trace Elements Hazardous waste extraction
Radiological Characterization	Coal Gasifier slag Sulfur recovery tail gas Accumulator discharge to wastewater treatment Treated effluent/Disposal pond & monitoring wells Solids to landfill (from wastewater treatment)	Ra-226 Ra-228
Medical Surveillance	Operating personnel (individual) Maintenance personnel (individual)	Preplacement physical examinations Periodic physical examinations Transfer/Termination physical examinations Followup physical examinations
Basic Industrial Hygiene	Operating personnel (individual) Maintenance personnel (individual) Employee work stations (ambient air)	CO H_2S COS Particulates Aromatic Hydrocarbons

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[a] NH_3, NO_2, and NO_3, organic N, TDS, TSS, VSS, BOD_5, alkalinity, COD, S^-, anide, TOC, formate. Also may include Ca, Mg, SO_4, SiO_2, PO_4

to be performed on the samples. These analyses will help to evaluate the environmental impact of our project and also may serve as a guide in evaluating the impact of future gasification projects. For instance, we fully expect that the slag studies will show that the slag is nonhazardous and should be handled similarly to the bottom ash from a coal-fired power plant.

The first four items in Table 2 covering the area of gaseous emission, water and solid discharge, and radiological characterization affect the health and welfare of the community beyond the plant boundary limits and as such are tremendously important. However, the studies listed here are routine and could be expected to be carried out in any program similar to the Ammonia from Coal Project.

The last two items deserve a closer look. The purpose of the medical surveillance and the industrial hygiene programs is first, to protect the workers assigned to the TVA Ammonia from Coal Project and second, to gain knowledge to answer the persistent questions concerning the health and safety of workers exposed to the coal gasification environment in general.

The medical program, developed by TVA's medical staff, includes a series of medical examinations. The first examination or preplacement examination of the candidate workers was made to determine preexisting conditions that might be adversely affected by work in the ACP. These people were advised of their conditions and counseled regarding methods of protection. Particular emphasis was placed on evaluating the condition of the skin, respiratory tract and genitourinary tract. Also, high quality color photographs were made of the exposed skin of the face, neck, hands, and any suspicious lesion or other skin problem areas. Periodic examinations will be made at not more than 12-month intervals. These will be complete physical examinations similar to the preplacement examinations. Termination and/or transfer examinations will also be essentially the same as the preplacement examination. In addition, followup examinations of former ACP employees may be made on a voluntary basis as part of an epidemological study of the employees. The epidemological study will involve pairing the ACP workers as a group with two other similar groups (comparable sex, age). One, a similar group of workers with histories of work in chemical plants except for this group's lack of exposure to the gasification environment. The second comparative group will have "clean" histories with no exposure in chemical plants. Statistical analysis will include a comparison between the two control groups and the ACP workers to determine the contribution, if any, of the gasifier environment to adverse health effects of exposed workers.

The primary objective of the ACP industrial hygiene program is to protect ACP employees from developing occupational diseases during the operation of the projects and at any time in the future. But, because of the demonstration nature of the ACP, another goal is to determine as completely as possible any health and safety hazards associated with the process. This overall assessment is expected to supply data for future coal conversion projects.

The possible hazardous agents that are of interest from an industrial hygiene standpoint which might be found in the environment and their maximum limits for unprotected workers are listed in Table 3.

Table 3 POSSIBLE HAZARDOUS AGENTS AND THEIR STANDARDS

AGENT	STANDARD (8 hr. TWA)
CARBON MONOXIDE	50 ppm[a]
HYDROGEN SULFIDE	10 ppm[a]
CARBONYL SULFIDE	(no standard)
COAL DUST	2 mg/m^3[b]
AROMATICS	10 ppm as benzene[b]
COAL TARS	0.2 mg/m^3 as benzene soluble fraction[b]
NOISE	90dBA[b]
HEAT	30°C WBGT (Wet bulb globe temperature)[a]

[a] Source: American Conference of Government Industrial Hygienists

[b] Source: Department of Labor, Occupational Health and Safety Administration

As a result of review of the plans and specifications for the gasification facilities by industrial hygiene personnel, control measures such as area monitors with audible alarms for carbon monoxide and hydrogen sulfide have been or will be built into the physical plant. Other control measures identified so far through the review process are: personnel protective equipment such as protective clothing, hearing protection, and safety glasses; positive pressure ventilation in control and analysis rooms; and provision of deluge showers and eye baths.

Before the initial startup of the ACP facilities, a walk-through inspection and evaluation of the plant was conducted. Area monitors and alarm systems were tested; control systems were evaluated; and procedures for the personal hygiene, protective clothing, and protective equipment were reviewed. The plant operational procedures will be reviewed periodically to evaluate their health and safety impacts.

A concentrated effort was begun during startup and will continue through preliminary operation of the ACP facilities to identify and measure hazardous agents produced by the operation of the facilities and equipment. Individual worker environment is being sampled by portable devices attached to the individual. Area samples are taken by fixed, automatic sampling stations located at strategic points throughout the plant. Samples from these sources are being analyzed in an attempt to identify unexpected as well as expected agents that could be generated. A statistically valid number of samples will be taken for each agent so that the confidence level will be maintained. This means that the individual worker environment probably will have to be sampled several times during the startup phase. If during the initial survey an unexpected hazardous situation is discovered, additional sampling will be scheduled.

Results from the initial survey will be evaluated and will serve as the basis for developing a secondary workplan that will cover all future industrial hygiene activities for ACP. The secondary workplan will cover at least the following items: the hazardous agents that will be periodically measured; the employees' exposure history; and the decision points concerning protective clothing usage. The workplan will be a dynamic guideline that will be subject to continuous change depending on the requirements of the ACP program.

The list of activities discussed above for the medical and industrial hygiene studies on the ACP is by no means complete. However, it does cover the major items of interest and indicates the degree of health protection and surveillance that is built into the ACP program. We anticipate that hindsight will show that we have considerable overprotection and overcaution in this area, but at this stage we are taking no chances.

ENVIRONMENTAL CONTROL OPTIONS FOR SYNFUEL PROCESSES

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Ultimately, the large scale production of synfuels from U.S. coal and oil shale will become a reality. The U.S. Department of Energy (DOE) has a charge to foster the commercialization of energy conversion technology that is environmentally acceptable. "Environmental acceptability" is perceived to extend beyond meeting environmental compliance standards at a given plant and to include the "acceptability" of subtle, longterm health and ecological effects and the composite of low level environmental effects associated with an aggregate of synfuel installations. DOE has a hierarchy of site-specific environmental assessments integral to DOE development and demonstration activity. The objective of these assessments is to provide a data base for a determination of environmental readiness by the Assistant Secretary for Environment. An evaluation of the adequacy of the environmental control technology is a key component of these determinations.

In assessment of control adequacy, many alternative approaches present themselves. Some of these control options result from a natural synergism of combining process needs; for example, an auxiliary power plant that recovers flue gas SO_2 in a concentrated stream can be advantageously coupled to H_2S recovery from the conversion process to produce by-product sulfur via Claus, or an entrained type gasifier can be included with a series of Lurgi gasification units to handle rejected coal fines and oxidize highly contaminated condensate wastewaters. Other control options follow from making controls more cost-effective and/or environmentally superior. Wastewater reuse to extinction (zero discharge) and the catalytic incineration of process tail gases are examples of improvements over conventional technology. In the case of small, site oriented industrial gasifiers, process simplicity and reliability are a driving force for improved controls or the absence thereof; for example, in-gasifier sulfur scavenging to eliminate subsequent H_2S cleanup or "dry-quenching" of product gas to eliminate the difficulty of wastewater treatment.

This presentation will overview a number of select environmental control options whose technical and economic feasibility has been recently established. The direction that future resultant control technology is expected to take will be outlined.

ENVIRONMENTAL CONTROL OPTIONS FOR SYNFUEL PROCESSES

INTRODUCTION

There has been considerable activity within the Department of Energy recently with regard to synfuels related initiatives. Some of this proliferation results from synfuel process development activity, which has been a long time in being and is now reaching the critical pilot plant or demonstration phase (Figure 1). However, much of this activity stems from industrial response to DOE's alternative fuels initiative (Figure 2). Most of these synfuel projects are in various stages of engineering and design. The alternative fuels efforts include both feasibility studies (preliminary design efforts) and cooperative agreements to share preconstruction and construction costs.

To one who has been "exposed" to these designs, several premises become clear:

- the energy conversion process design is tailored to the feedstock, end-product mix, and specific site;
- the environmental control technology is integrated with the process (end-of-the-pipe philosphy does not generally prevail); and
- a large number of environmental control options exist.

The innovative integration of environmental controls with the conversion processes is a relatively new area of process design. This innovation has resulted in new and different controls required as a result of recent and evolving environmental standards (especially in the synfuels area). The evolution of controls with the technology facilitates a beneficial synergism that can be missed if considered mutually independent. The development of such control synergisms can involve different sections of the plant and be based on the integration of both multimedia and multipollutant interactions. It has long been the contention of the Assistant Secretary for Environment that environment control development should be handled integral to the technologies.

In this symposium Pollution Control Guidance Documents (PCGD) will be discussed. These documents attempt to develop an environmental data base for synfuels process configurations. A number of representative plant configurations have been selected and preferred control options concomitantly delineated. These generalized studies reinforce the fact that a large number of control options exist for a given synfuel process. Because of these many options and their different effect on overall process characteristics, it is indeed a challenging and difficult task to specify a "Best Available Control Technology" (BACT) for these emerging technologies. Perhaps it is best to return to the BACT concept after a brief discussion of control options.

In this presentation I would like to develop an appreciation for the complexity of the control systems and their high variability as reflected in recent designs, to stress the potential benefits resulting from integrating multimedia controls to the conversion process, and to outline some control options that possess an economic incentive for further development. The intent is to provide an overview of the numerous control options that are emerging and the direction future controls may take. The discussion will be confined to coal based synfuel processes and the conversion process per se, however, it may be considered representative of other areas such as oil shale and biomass conversion.

FIGURE 1. MAJOR DOE FOSSIL ENERGY DEMONSTRATION ACTIVITY – COAL SYNFUEL PROCESSES (SEPT 1980)

	PROJECT	LOCATION	COAL DEMAND Ton/Day	MAJOR PRODUCTS	STATUS
Gasification	Gasifiers-in-Industry	Duluth, Minn.	75	Heating Gas, Fuel Oil	Operative
	Memphis	Memphis, Tenn.	3200	Medium Btu Fuel Gas, SNG	In Detailed Design
	Grace	Baskett, Ky.	2300	Ammonia	In Preliminary Design (Reoriented toward Methanol and Mobil-M Gasoline)
	Conoco	Noble County, Ohio	1080	SNG	In Detailed Design
	ICGG	Willisville, Ill.	2300	SNG, Fuel Oil	In Detailed Design
Liquefaction	SRC I	Newman, Ky.	6000	Solid Boiler Fuel	In Detailed Design
	SRC II	Morgantown, W.Va.	6000	Fuel Oil	In Detailed Design
	H-Coal	Catlettsburg, Ky.	200-600	Fuel Oil, Syncrude	Pilot-Plant in Shakedown
	EDS	Baytown, Tex.	250	Fuel Oil, Syncrude	Pilot Plant in Shakedown

FIGURE 2. SELECT COAL SYNFUELS ALTERNATIVE FUELS SOLICITATION — FEASIBILITY STUDIES AND COOPERATIVE AGREEMENTS (JULY 1980)

	CONTRACTOR	POTENTIAL SITE	FUNDING REQUEST*	MAJOR PRODUCT
Feasibility Studies	W.R. Grace	Moffat Co., Colo.	$ 786,477	Methanol
	Clark Oil & Refining	S. Ill.	$4,000,000	Gasoline
	General Refractories	Florence, Ky.	$ 922,555	Low Btu Industrial Fuel Gas
	Houston Natural Gas	Covent, La.	$3,260,000	Fuel Grade Methanol
	Central Me. Power	Waldo Co., Me.	$3,624,558	Medium Btu Gas for Combined Cycle
	EG&G	Fall River, Mass.	$4,000,000	Combined Cycle Power and Methanol
	Crow Tribe	East Billing, Mont.	$2,729,393	SNG
	Nakota Co.	Dunn, N. Dak.	$4,000,000	Methanol
	Phil. Gas Works	Phil., Penn.	$1,168,108	Medium Btu Gas
	Celanese Corp.	Bishop, Tex.	No Cost	Syngas
	Transco Energy	Calvert, Tex.	$1,874,005	Medium Btu Gas
	Union Carbide	Houston, Tex.	$3,945,676	Low/Medium Btu Gas
	Hamphire Energy	Gillette, Wyo.	$4,000,000	Gasoline
Cooperative Agreements	Texas Eastern Synfuels	Henderson, Ky.	$24.3M	SNG—44%, Transportation Fuel—30%
	Great Plains Gasification	Beulah, N. Dak.	$22M	SNG
	Wycoal	Douglas, Wyo.	$13.1M	SNG

*To be Negotiated

CONTROL OPTIONS

In considering the environmental impact of coal conversion, the total process train should be taken into consideration (coal mining, beneficiation, transporation, preparation, synfuels production, and product upgrading, distribution and end-use). The conversion process is typically supported by an auxiliary boiler/power plant. At the synfuel plant site, the auxiliary boiler plant is normally the major source of emission of criteria pollutants.

The major synfuel conversion processes, gasification and liquefaction (direct and in-direct), are environmentally similar relative to inorganic pollutants, i.e., sulfur, NO_x precursors, particulates, solid wastes, trace elements, etc. With regard to the production of heavy organics, there is a wide variation between processes, not so much as to "type" of organics, but to degree, since a wide range of aromatic based tars and oils are typically produced. However, there can be a marked difference in the bioactivity of the liquid fractions; as a disproportionate portion of mutagenicity (which is indicative of carcinogenicity) has been found to reside in high boiling primary aromatic amines which can vary widely between processes. Entrained gasification, being a high temperature process, cracks most of the organics thereby producing a product gas and quench water which is nearly devoid of heavy organics. This is in contrast to the heavily organic laden condensate/quench waters associated with direct, low temperature gasification processes and/or liquefaction. For catalytic processes, the effect of spent catalyst on solid and aqueous wastes varies process to process.

Environmental control options are conventionally segregated into types which deal specifically with gaseous, liquid and solid pollutants. This follows in part from the environmental legislation which is primarily concerned with impact on the accpetor media, e.g., air, water, and land. However, in evaluating a control option, effects on other media must be taken into consideration. Ideally, the pollution control process is fully integrated with the conversion process to take advantage of economics of energy consumption, reduced pollutant production, water reuse potential and by-product production.

Complexity and Variability of Environmental Controls

Major potential pollutant sources which require the use of control processes are:

1. flue gas from auxiliary power plant/boilers
2. sulfur containing tail gases from acid gas separation
3. wastewater from multiple sources (product gas quench, coal pile runoff, sanitary sewer, etc.)
4. auxiliary power plant/boiler solids (bottom ash, fly ash, scrubber sludge)
5. conversion process solids (ash/slag, wastewater sludges, spent catalyst, etc.)

power plant/boiler flue gas -

EPA, DOE, and industry continue to develop a large inventory of control options to reduce the emissions of sulfur oxides, nitrogen oxides and particulates from the combustion of coal. For sulfur control, coal beneficiation and lime/limestone flue gas desulfurization (FGD) have received primary emphasis and are considered commercial processes. A number of other alternatives are at various stages of development and demonstration, e.g., double alkali, dry-FGD, fluidized bed combustion (FBC), and co-generation. In the area of NO_x control, combustion modification including low excess air, staged combustion, and burner modifications appears capable of meeting the emission requirements specified by current New Source Performance Standards (NSPS). NSPS particulate release standards (0.03 lb/MBtu) can be met by deploying enhanced electrostatic precipitators or fabric filters. It is emphasized that these NSPS apply to compliance criteria and are current. Future changes can be expected in the regulations concomitant with major synfuels activities over the next 10-20 years.

tail gases -

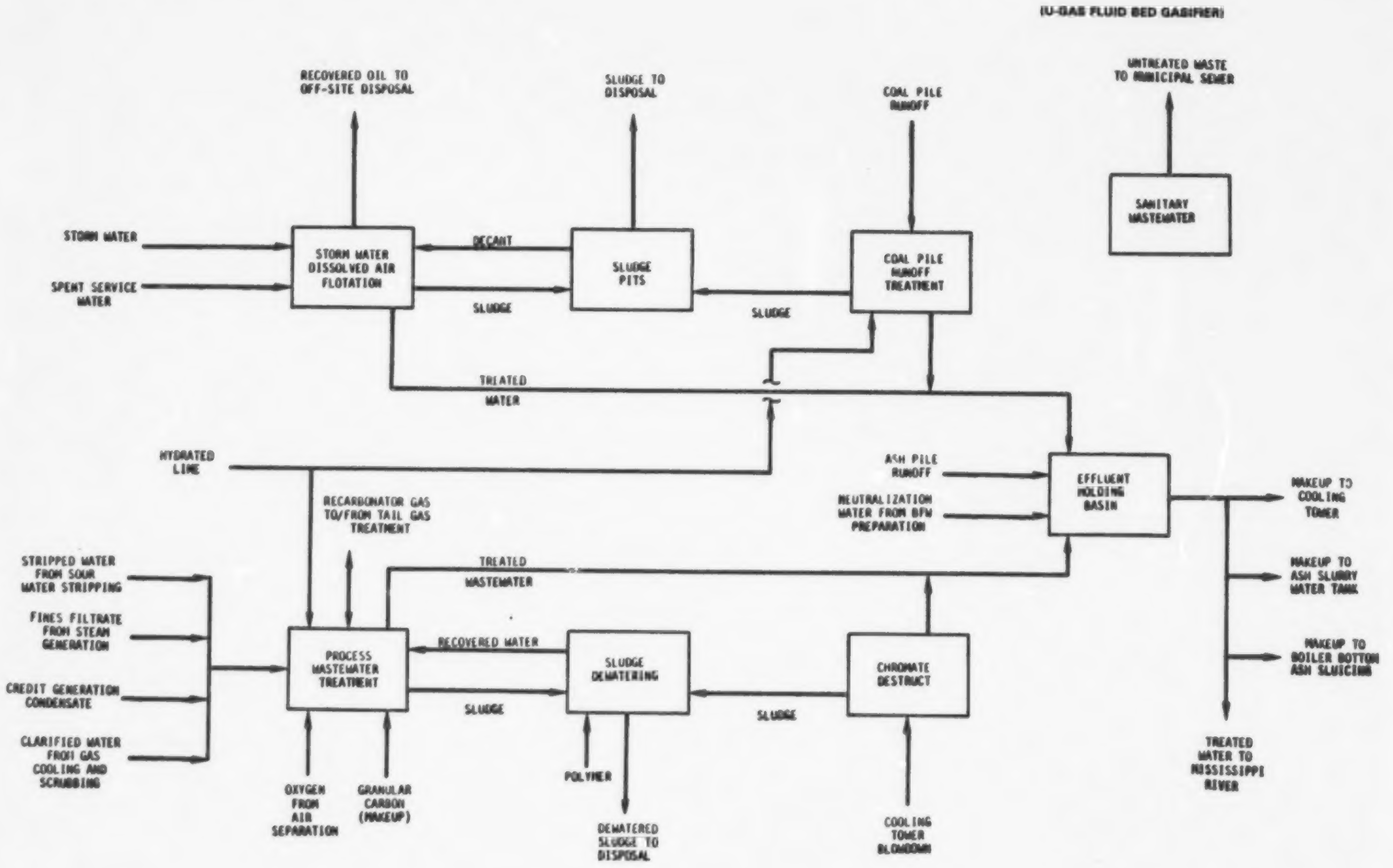
The gaseous sulfur compounds generated during the coal conversion process (primarily H_2S, some COS, CS_2, mercaptans, and thiophenes) are generally removed along with CO_2 by the acid gas treatment train. The acid gases may be non-selectively absorbed and partitioned into a H_2S enriched stream (40-60%) and a H_2S lean stream (2-10%); the enriched and lean streams are typically routed to a Claus unit and a selective absorption unit, respectively, for sulfur recovery (Figure 3). The nominal CO_2 tail gases from these systems generally contain trace residual sulfur--the Claus system removes all but a few percent of the H_2S, while the absorption system can produce a tail gas with about 100 ppm H_2S. Incineration represents the preferred treatment for the H_2S-depleted streams which also may contain some low level hydrocarbons. Stringent sulfur emission standards could necessitate additional H_2S absorption prior to incineration or scrubbing of the incineration flue gas with a conventional FGD system. In any event, it is apparent that high H_2S removal efficiency ($>$97%) can be confidently achieved with existing commercial equipment.

wastewater -

Coal gasification and liquefaction typically produce a highly contaminated "condensate" water which represents a by-product of the conversion reaction, extra steam for cooling, a quench for direct cooling and scrubbing product gases, etc. A wide range of organic loading is experienced; however, compositions tend to be similar with phenolic compounds usually predominating. Condensate waters originating from a high temperature process (non-tar producer) can be essentially devoid of organic material.[1] Most plants tend to design for "zero" discharge of condensate waters, that is, no condensate water is discharged to a surface acceptor; however, such water may be rejected to the atmosphere through evaporation and concentrated aqueous wastes, or may be disposed of via land-fill, ash surface wet-down, deepwell injection (in accordance with applicable underground injection control regulations), etc. Some process schemes consume the contaminated water as recycle to gasification. In addition to condensate waters, various blowdowns produced from feedwater treatment, boiler and cooling tower operation, coal pile runoff, and sanitary wastes are generally integrated into the overall wastewater treatment train. For example, if one examines the design of the wastewater treatment trains for the major gasification projects DOE is involved with, one finds a wide variation of process trains (Figures 4-8). The wastewater treatment options may involve the combination of streams to enhance treatability and evaporation of salt laden blow-downs. The variability between these wastewater treatment schemes is stressed.

FIGURE 3. COMMERCIAL ADSORPTION PROCESSES FOR CONTROL OF HYDROGEN SULFIDE

Process	Absorbent	Type of Absorbent	Temp. °F	Pressure	Efficiency of S Removal		Absorbent Characteristics				Form of Sulfur Recovery
					% H_2S Influent	Effluent H_2S ppm	Life	Regeneration	Selectivity Toward	Makeup Rate	
Chemical Solvent Type:											
1. MEA	Monoethanolamine	Aqueous Solution	80 to 120	Insensitive to Variation in Pressure	99	~100		Thermal	Forms nonregen. comp. with COS, CS_2	50 to 100%	As H_2S gas
2. DEA	Diethanolamine	Aqueous Solution	100 to 130	Insensitive to Variation in Pressure	99	~100		Thermal	Absorbs CO_2 does not absorb COS, CS_2	<5%	As H_2 gas
3. TEA	Triethanolamine	Aqueous Solution	100 to 180	Insensitive to Variation in Pressure	99	~100		Thermal	H_2S	<5%	As H_2S gas
4. Alkazid	Potassium Dimethylamino Acetate	Aqueous Solution	70 to 120	Insentive to Variation in Pressure 1-80 Atm	99	~100		With steam	H_2S		As H_2S gas
5. Benfield	Activated Potassium Carbonate Solution	Aqueous Solution	150 to 250		99	H_2S + COS ~100	Unlimited. No degradation	With steam	H_2S is high		As H_2S gas
6. Catacarb	Activated Potassium Carbonate Solution	Aqueous Solution	180 to 250	Insensitive to Variation in Pressure generally >300 psi	99	H_2S + COS		With steam	H_2S partial also absorbs COS, CS_2	<5%	As H_2S gas
Physical Solvent Type:											
7. Sulfinol	Sulfolane + Diisopropanamine	Organic Solvent	80 to 120	High Pressure Preferred	99	H_2S + COS ~100		Low pressure heating or with steam	H_2S and also absorbs COS, CS_2 and mercaptans		As H_2S gas
8. Selexol	Polyethylene Glycol Ether	Organic Solvent	20 to 80		99	H_2S + COS ~100			H_2S, also absorbs COS		As H_2S gas
9. Rectisol	Methanol	Organic Solvent	<0		99	~100			H_2S		
Direct Conversion:											
10. Stretford	Na_2CO_3 + Anthraquinone Sulfonic Acid	Alkaline Solution			99.9	~10			H_2S	50 to 100%	Elemental sulfur
11. Townsend	Triethylene Glycol	Aqueous Solution	150 to 250		99.9	~10			H_2S		Elemental sulfur
Drybed Type:											
12. Iron Sponge	Hydrated Fe_2O_3	Fixed Bed	70 to 100		99	H_2S + COS ~100			H_2S and also towards COS, CS_2 and mercaptans		Elemental sulfur



(U-GAS FLUID BED GASIFIER)
RECOVERED OIL TO OFF-SITE DISPOSAL
SLUDGE TO DISPOSAL
COAL PILE RUNOFF
UNTREATED WASTE TO MUNICIPAL SEWER
SANITARY WASTEWATER
STORM WATER
SPENT SERVICE WATER
STORM WATER DISSOLVED AIR FLOTATION
DECANT
SLUDGE
SLUDGE PITS
SLUDGE
COAL PILE RUNOFF TREATMENT
TREATED WATER
HYDRATED LIME
ASH PILE RUNOFF
NEUTRALIZATION WATER FROM BFW PREPARATION
EFFLUENT HOLDING BASIN
MAKEUP TO COOLING TOWER
RECARBONATOR GAS TO/FROM TAIL GAS TREATMENT
TREATED WASTEWATER
MAKEUP TO ASH SLURRY WATER TANK
STRIPPED WATER FROM SOUR WATER STRIPPING
FINES FILTRATE FROM STEAM GENERATION
CREDIT GENERATION CONDENSATE
CLARIFIED WATER FROM GAS COOLING AND SCRUBBING
PROCESS WASTEWATER TREATMENT
RECOVERED WATER
SLUDGE
SLUDGE DEWATERING
SLUDGE
CHROMATE DESTRUCT
MAKEUP TO BOILER BOTTOM ASH SLUICING
OXYGEN FROM AIR SEPARATION
GRANULAR CARBON (MAKEUP)
POLYMER
DEWATERED SLUDGE TO DISPOSAL
COOLING TOWER BLOWDOWN
TREATED WATER TO MISSISSIPPI RIVER

FIGURE 4. WASTEWATER TREATMENT SYSTEM — MEMPHIS INDUSTRIAL FUEL GAS PLANT

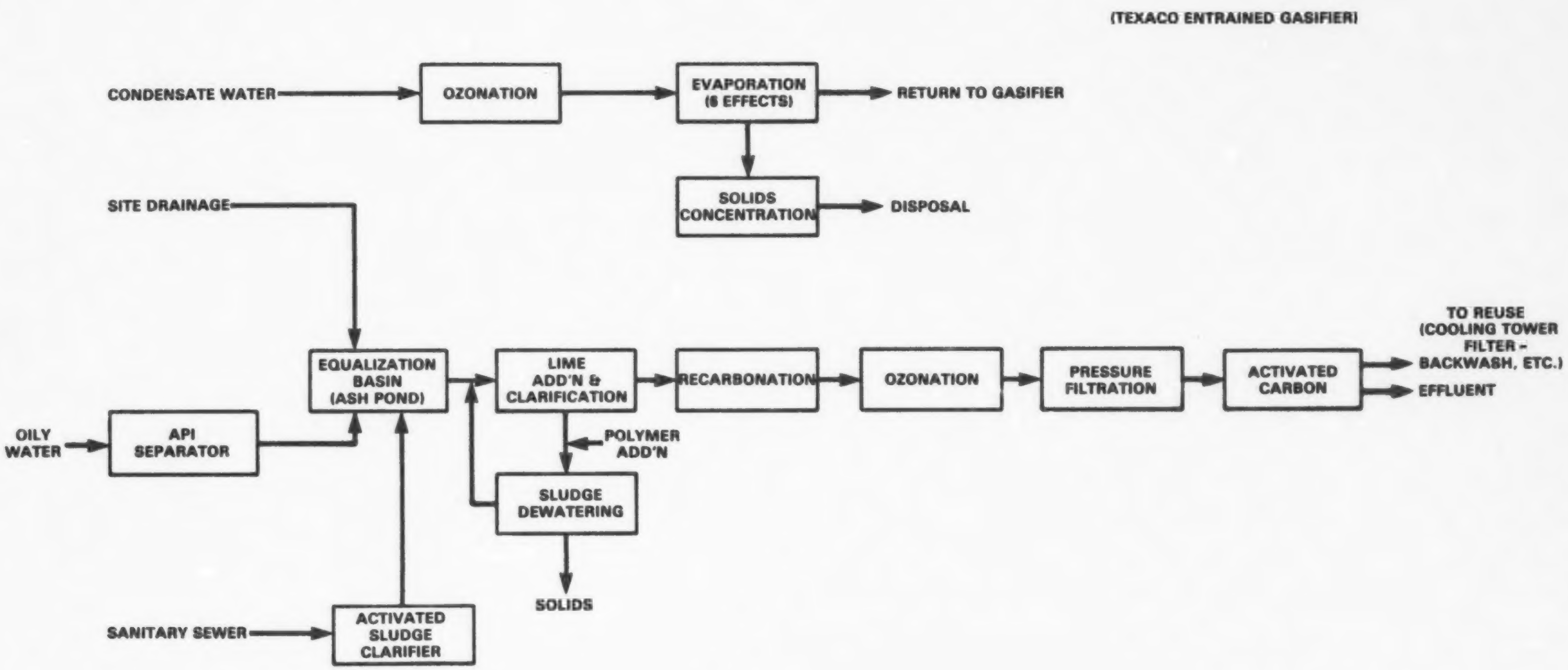

(TEXACO ENTRAINED GASIFIER)
CONDENSATE WATER
OZONATION
EVAPORATION (6 EFFECTS)
RETURN TO GASIFIER
SOLIDS CONCENTRATION
DISPOSAL
SITE DRAINAGE
OILY WATER
API SEPARATOR
EQUALIZATION BASIN (ASH POND)
LIME ADD'N & CLARIFICATION
POLYMER ADD'N
SLUDGE DEWATERING
SOLIDS
SANITARY SEWER
ACTIVATED SLUDGE CLARIFIER
RECARBONATION
OZONATION
PRESSURE FILTRATION
ACTIVATED CARBON
TO REUSE (COOLING TOWER FILTER - BACKWASH, ETC.)
EFFLUENT

FIGURE 5. WASTEWATER TREATMENT SYSTEM — GRACE AMMONIA DEMO PLANT
(CURRENTLY IN REDESIGN TO PRODUCE METHANOL AND M-GASOLINE)

(BRITISH GAS/LURGI SLAGGING FIXED BED GASIFIER)

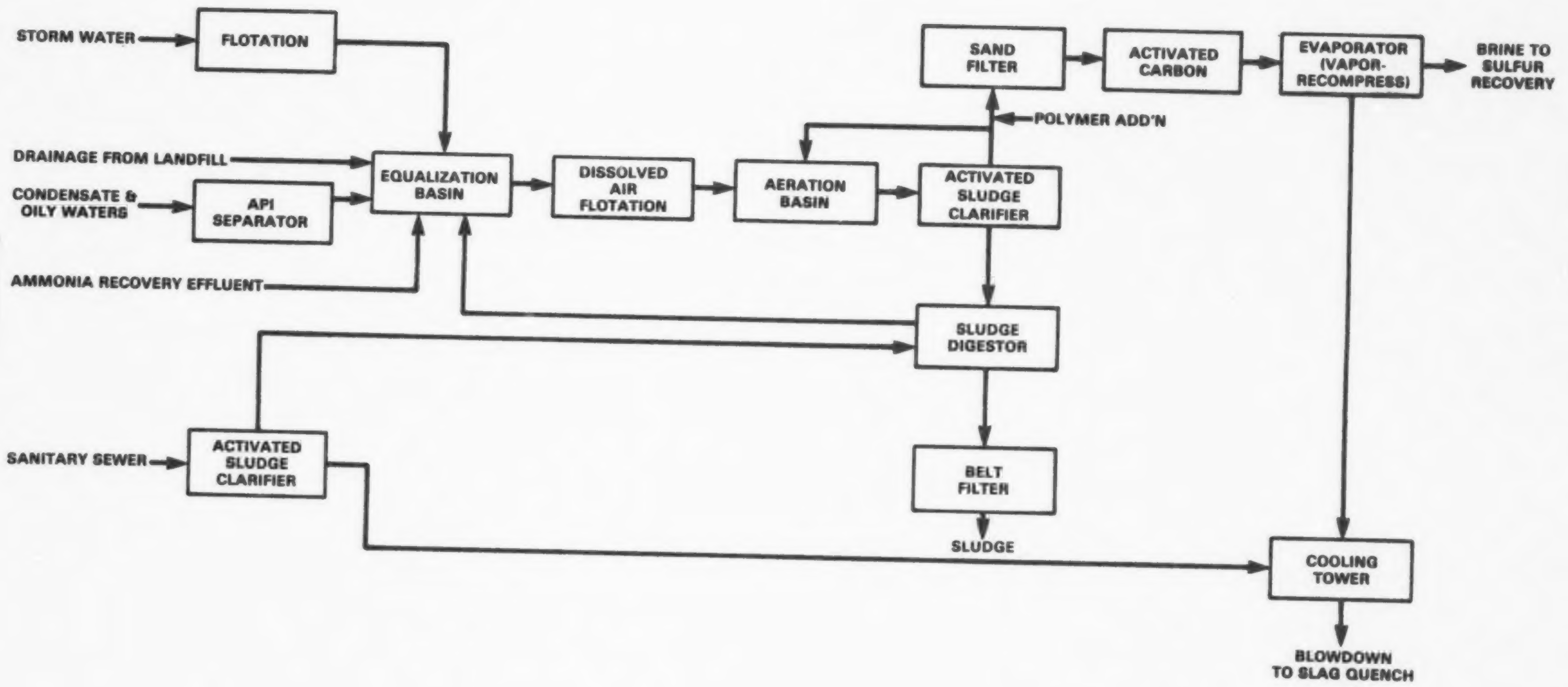

STORM WATER
FLOTATION
DRAINAGE FROM LANDFILL
CONDENSATE & OILY WATERS
API SEPARATOR
AMMONIA RECOVERY EFFLUENT
EQUALIZATION BASIN
DISSOLVED AIR FLOTATION
AERATION BASIN
ACTIVATED SLUDGE CLARIFIER
POLYMER ADD'N
SAND FILTER
ACTIVATED CARBON
EVAPORATOR (VAPOR-RECOMPRESS)
BRINE TO SULFUR RECOVERY
SLUDGE DIGESTOR
BELT FILTER
SLUDGE
SANITARY SEWER
ACTIVATED SLUDGE CLARIFIER
COOLING TOWER
BLOWDOWN TO SLAG QUENCH

FIGURE 6. WASTEWATER TREATMENT SYSTEM – CONOCO SNG DEMO PLANT

(COGAS STAGED PYROLYSIS GASIFIER)

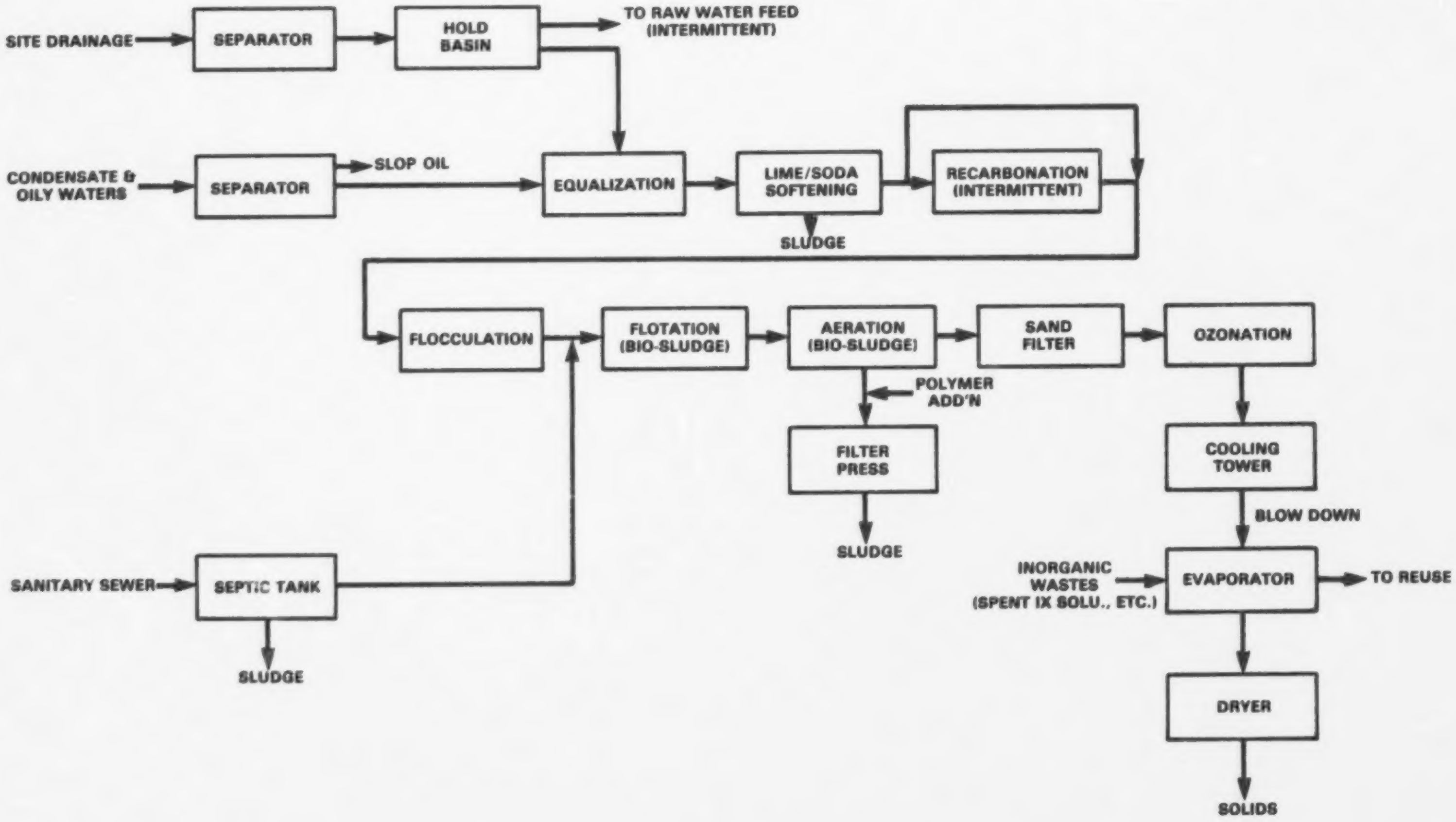
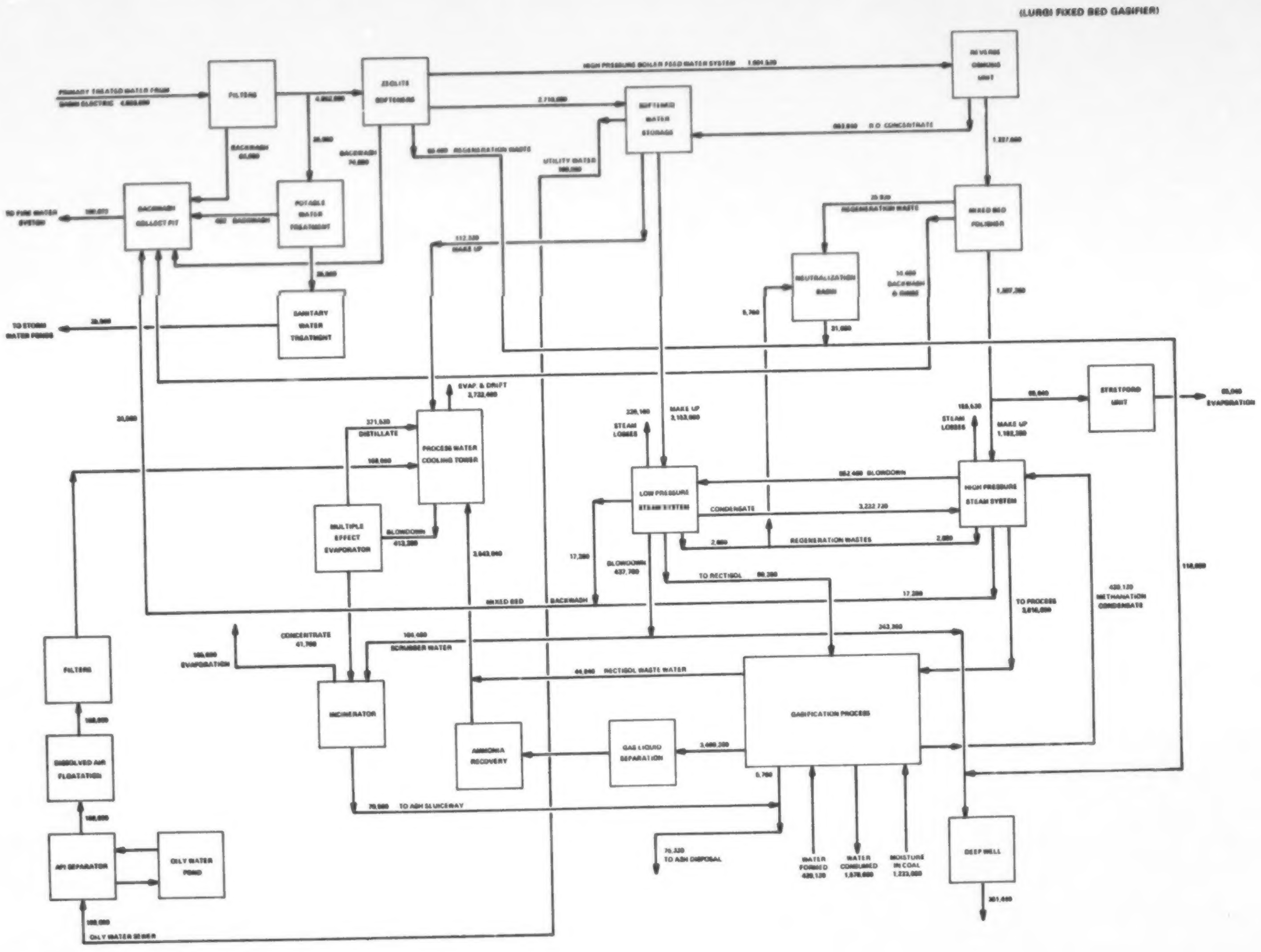

SITE DRAINAGE
SEPARATOR
HOLD BASIN
TO RAW WATER FEED (INTERMITTENT)
CONDENSATE & OILY WATERS
SEPARATOR
SLOP OIL
EQUALIZATION
LIME/SODA SOFTENING
SLUDGE
RECARBONATION (INTERMITTENT)
FLOCCULATION
FLOTATION (BIO-SLUDGE)
AERATION (BIO-SLUDGE)
SAND FILTER
OZONATION
POLYMER ADD'N
FILTER PRESS
SLUDGE
COOLING TOWER
BLOW DOWN
SANITARY SEWER
SEPTIC TANK
SLUDGE
INORGANIC WASTES (SPENT IX SOLU., ETC.)
EVAPORATOR
TO REUSE
DRYER
SOLIDS

FIGURE 7. WASTEWATER TREATMENT SYSTEM — ICGG SNG DEMO PLANT


(LURGI) FIXED BED GASIFIER)
PRIMARY TREATED WATER FROM
BASIN ELECTRIC 4,800,000
FILTERS
4,862,000
ZEOLITE SOFTENERS
HIGH PRESSURE BOILER FEED WATER SYSTEM 1,601,520
REVERSE OSMOSIS UNIT
2,710,080
SOFTENED WATER STORAGE
BACKWASH 61,000
26,000
BACKWASH 70,000
60,480 REGENERATION WASTE
UTILITY WATER 180,000
R.O. CONCENTRATE
1,227,600
TO FIRE WATER SYSTEM
BACKWASH COLLECT PIT
420 BACKWASH
POTABLE WATER TREATMENT
112,320 MAKE UP
25,920 REGENERATION WASTE
MIXED BED POLISHER
26,000
NEUTRALIZATION BASIN
10,400 BACKWASH & RINSE
5,760
1,207,280
TO STORM WATER PONDS
SANITARY WATER TREATMENT
31,680
20,000
EVAP. & DRIFT 2,722,480
371,520 DISTILLATE
168,000
PROCESS WATER COOLING TOWER
226,160 STEAM LOSSES
MAKE UP 3,153,000
186,630 STEAM LOSSES
MAKE UP 1,182,280
69,840
STRETFORD UNIT
69,840 EVAPORATION
MULTIPLE EFFECT EVAPORATOR
BLOWDOWN 412,280
3,043,040
17,280
BLOWDOWN 437,760
LOW PRESSURE STEAM SYSTEM
852,480 BLOWDOWN
CONDENSATE
3,222,720
HIGH PRESSURE STEAM SYSTEM
2,880
REGENERATION WASTES
2,880
TO RECTISOL 86,280
MIXED BED
BACKWASH
17,280
TO PROCESS 3,816,000
420,120 METHANATION CONDENSATE
118,800
FILTERS
166,600 EVAPORATION
CONCENTRATE 41,760
166,480 SCRUBBER WATER
243,360
44,640 RECTISOL WASTE WATER
GASIFICATION PROCESS
168,000
DISSOLVED AIR FLOATATION
INCINERATOR
AMMONIA RECOVERY
GAS LIQUID SEPARATION
3,460,200
5,760
168,000
API SEPARATOR
OILY WATER POND
70,560 TO ASH SLUICEWAY
70,320 TO ASH DISPOSAL
WATER FORMED 420,120
WATER CONSUMED 1,578,600
MOISTURE IN COAL 1,223,000
DEEP WELL
301,440
168,000
OILY WATER SEWER

ALL FLOWS IN GALLONS/DAY
ALL FLOWS ARE FOR PHASE I ONLY — DOUBLE FLOWS FOR FULL PLANT

FIGURE 8. SCHEMATIC OF WATER SYSTEM FLOW ANG COAL GASIFICATION COMPANY (REVISED OCTOBER 31, 1979)

One common characteristic of the wastewater systems that must handle an organically charged condensate water (Conoco, ICGG, and ANG) is that there is "zero discharge" for this stream. The rationale for the selection of the "zero discharge" alternative with respect to condensate waters is that while activated sludge tends to be a universal process for adequately treating condensate waters to effluent qualities reflective of current regulations, the nature of these wastewaters, i.e., high organic loading, toxicity of certain compounds, presence of refractory organics, heavy metals and trace elements, causes uncertainty with respect to the evolving Federal regulations resulting from the Toxic Substance Control Act (TSCA) and the Resource Conservation Recovery Act (RCRA). While the technical feasibility of additional steps to the conventional activated sludge train for controlling effluents to more stringent standards has been demonstrated, the treatment processes become more complicated and costly.

solid wastes -

The major solids produced by coal conversion facilities obviously result from the mineral content of the coal feedstock. The characteristics (state) of the slag or ash associated with the conversion process are dependent on the nature of the process per se, since high temperature entrained gasification produces a relative inert glassy material while non-slagging fixed bed gasifiers produce an ash. Preliminary leaching tests indicate that both forms have weathering properties similar to power plant bottom ash. Depending on the method of controlling SO_2 emissions, there may be considerable scrubber sludge from the auxiliary power plant which typically gets disposed of along with wastes from the conversion process. Wastewater sludges, salts from evaporator ponds and/or concentration equipment, spent catalysts and absorbents are representative of relatively low volume secondary wastes that are likely to require special treatment in order to be disposed in a manner consistent with RCRA requirements. The individual treatment and/or disposal methods must be tailored to the specific waste and site.

Integration of Multimedia Controls within Coal Synfuel Processes

In incorporating the afore discussed controls into a plant design, a number of trade-offs exist, e.g., situations where by-products, contaminated water, spent solids, waste heat, etc. can advantageously be used within the process and/or environmental control area (Figure 9). A number of these "options" have appeared in process designs and the literature. Others have been "conjured up" to give some indication where innovative engineering might lead to improve the efficacy of the process. In my judgement, this is an area that deserves further analysis to determine the more promising options and their respective incentives.

One might ask "What are the economic incentives for some of the synergisms which have been projected?" That is, are they really worth the undertaking of the development and associated risk in the application? The answer to this question is best satisfied by a detailed trade-off analysis. However, one can develop a "feel" for potential savings. A very approximate breakdown of costs of environmental controls for a major coal synfuels facility is given in Figure 10.[2] Product costs are estimated to be in the neighborhood of \$5-8/MBtu for SNG, thus environmental controls should typically account for 10-20% of the total product cost. Reducing overall environmental control costs by say 50% (which is highly unlikely) would result in a saving of merely 5-10% in product costs, not a large incentive

FIGURE 9. CANDIDATE SYNERGISMS FOR COAL CONVERSION PROCESS AND ENVIRONMENTAL CONTROLS

ENVIRO CONTROL	SECONDARY CONTROL/ UNIT OP	SYNERGISM	POTENTIAL BENEFIT
Wastewater Concentration	Cooling Tower	Wastewater Conc-Heat Rejection	Precludes or Reduces Effluent Release, Reduces Raw Water Requirements
Wastewater Treatment	Water Reuse	High Quality Effluent from Treatment Train-Boiler Water Makeup and Process Water Requirements	Reduces Raw Water Requirements
Oil/Tar Disposal	Aux Heat/ Power	Combustion of Organics-Heat Recovery	Maintains Potentially Hazardous Material Within Plant Boundary
Tail Gas Control	Aux Power Combustor/FGD	Existing Boiler and Flue Gas Clean-up Train Used to Control Tail Gas HC and Sulfur Releases	Avoids Special Controls and Insures High Quality Emission
Vent Gas Control	Aux Power Combustor	Existing Boiler Used to Control Vent Gas HC Release in Lieu of Flare	Potentially Better Control Especially if Stack Gas Clean-up Practiced
Wastewater Incineration	Entrained Gasifier	Destruction of Organics, Conc of Solids-Provide Steam Req'mts	Avoids Elaborate Treatment Train to Produce High Quality Effluent
Wastewater Concentration	Aux Power FGD	Wastewater Conc-Makeup to Flue Gas Scrubber	Reduces Effluent Release and Raw Water Requirements
H_2S Recovery	Regenerative FGD, i.e. Dual Alkali	H_2S and SO_2 Control Combined in Claus Unit	No Scrubber Sludge, By-product Elemental Sulfur
Ash/Slag Disposal	FGD Sludge Disposal	Mutual Disposal	Alkaline Sludge will Discourage Trace Metal Leaching from Ash/Slag
Wastewater Treatment	FGD Sludge/ Slurry Disposal	Flocculation/Clarification-Combined Wastewater/FGD Sludge Disposal	Reduction of Wastewater Lime Req'mts
Wastewater Treatment	Oxygen Production	Relatively Cheap Oxygen Used to Abet Bioxidation and/or Ozone Production	Improved, Cost-Effective Treatment
Wastewater Disposal	Ash Cool Down	Wastewater Further Concentrates While Quenching Hot Slag	Facilitates Disposal of Wastewater Concentrate
Wastewater Disposal	Wetdown of Ash Piles and Mine Tailings	Wastewater Disposal-Control of Fugitive Emissions	Facilitates Disposal of Wastewater Concentrate, Dust Control and Mine Restoration
Wastewater Concentration	Heat Rejection	Wastewater Conc by Envaporation and/or Freezing Adsorption System-Low Quality Steam Utilization	Improved, Cost-Effective Wastewater Desalination and Reduction of Organics
Wastewater Treatment	Wastewater Stripping	Addition of Lime to the Wastewater Abets NH_3 Stripping and Flocculation/Clarification	More Complete NH_3 Stripping and Cost-Effective Use of Lime

FIGURE 10. ESTIMATE OF ENVIRONMENTAL CONTROL COSTS COAL SYNFUEL FACILITY

Overall process efficency assumed to be 65%
Auxiliary power plant assumed to use 20% coal input
Coal: 10,000 Btu/lb, 10% ash, 3.5% S

	Cost basis	¢/MBtu synfuel output		
Auxiliary power plant		low		high
SO_2 scrubbing	5-10 mills/kwhr	15	-	30
NO_x burner control	nil			
Particulates - bag house	1-2 mills/kwhr	3	-	6
Solid disposal (ash and sludge)	$10/ton		2	
Conversion Process[1]				
Sulfur[2]	10-20 ¢/MBtu	10	-	20
Tail gas incineration	5-10 ¢/MBtu	5	-	10
Wastewater treatment	$10-20/1000 gal	10	-	40
Slag disposal	$3-10/ton	2	-	6
		47	-	114

MBtu = 10^6 Btu

---

[1] excludes mining - environmental aspects included in cost of coal.
[2] in some instances high level removal required to preserve catalysis activity

from the perspective of the producer and potential risks incurred, if the control processes encounter difficulties and disrupt operations. However, if one looks at the incentive in absolute terms, for a single major facility, a 10¢/MBtu saving translates into \$7.5 M/yr. or \$200 M over the life of the facility. Savings of 10¢/MBtu in the environmental control area are not unrealistic. It is this driving force that has encouraged the study of the feasibility of improved environmental control options in DOE's Environmental and Safety Engineering Division (ESED).

Control Options Studied

As a result of a continuing assessment of environmental control adequacy within DOE/ESED, a number of candidate control options have become worthy of a determination of technical-economic feasiblity:

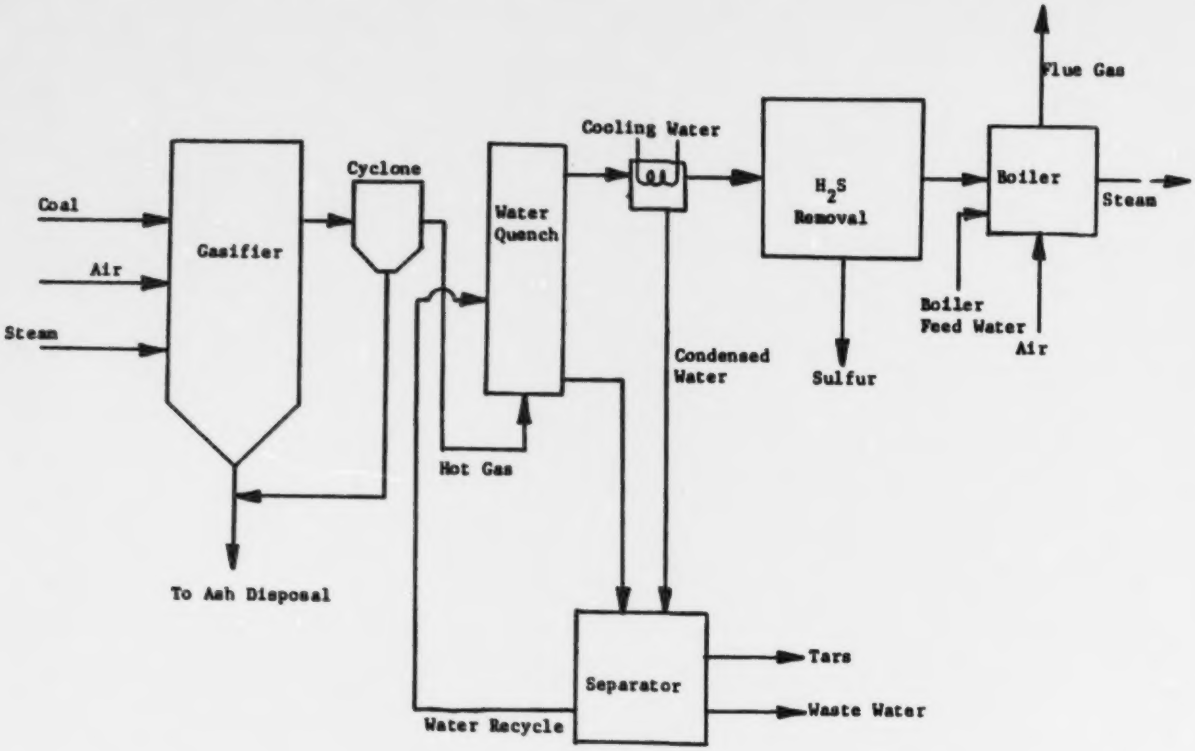
sulfur -

Sulfur absorption technology is well established and based on experience in the petroleum industry. There has been some minor concern for possible contamination of the absorption media with complex hydrocarbons, trace elements and dust; however, operating experience on coal gases indicate such effects can be accommodated.

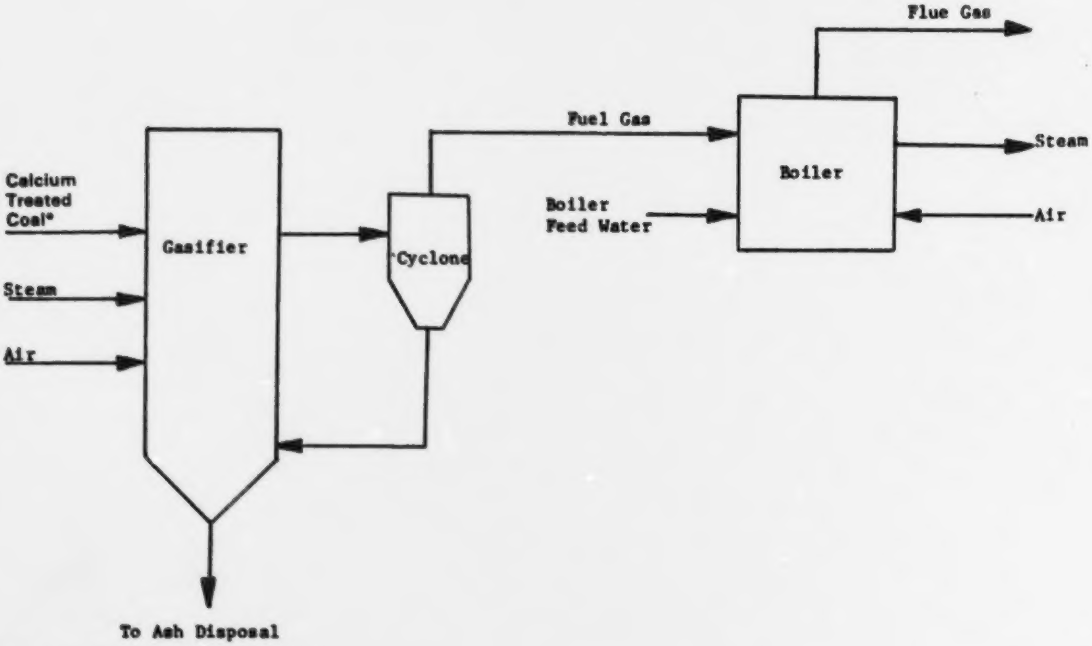
With the intent of simplifying the clean-up technology for an on-site industrial fuel gas producer, the control of sulfur within the gasifier proper using a calcium treated coal has been studied (Figures 11 and 12).[3] An important advantage of the use of a treated coal feedstock to small users is that it eliminates the environmental problems associated with the treatment and disposal of sludges and waste water generated from flue gas clean-up and fuel gas desulfurization. Another significant advantage to consider is the improved process reliability expected from this approach relative to product (fuel) gas cleanup and FGD options. The user simply needs a supply/inventory of treated coal to keep running or make a fuel switch. For those applications where intermittent operations are contemplated due to prime fuel curtailment, the use of treated coal would eliminate the need to operate and maintain a chemical scrubbing system.

Laboratory screening studies have demonstrated that a coal treated with CaO at ambient conditions can effectively remove sulfur and produce a low-sulfur fuel gas in a moving-bed, a fluidized-bed, or an entrained bed gasification system. The sulfur captured in the gasification ash is converted to essentially inert calcium sulfate for environmentally safe disposal. Sulfur removal efficiencies of calcium treated coal relative to untreated coal are shown in Figure 13.

A preliminary economic evaluation of "conversion to coal" (oil/gas backout) by typical industrial users has shown the treated coal to be competitive with the direct combustion of coal and with the gasification of untreated coal that require flue gas desulfurization and fuel (product) gas desulfurization respectively, for controlling sulfur emissions. Results of a preliminary cost evaluation of industrial steam generating systems with a peak load of 100,000 lb/hr steam and an average load of 60,000 lb/hr steam are presented in Figure 14 to compare various fuel-replacement/retrofit options.


Flue Gas
Cooling Water
Cyclone
Coal
Air
Steam
Gasifier
Water Quench
H_2S Removal
Boiler
Steam
Boiler Feed Water
Air
Condensed Water
Sulfur
Hot Gas
To Ash Disposal
Separator
Tars
Waste Water
Water Recycle

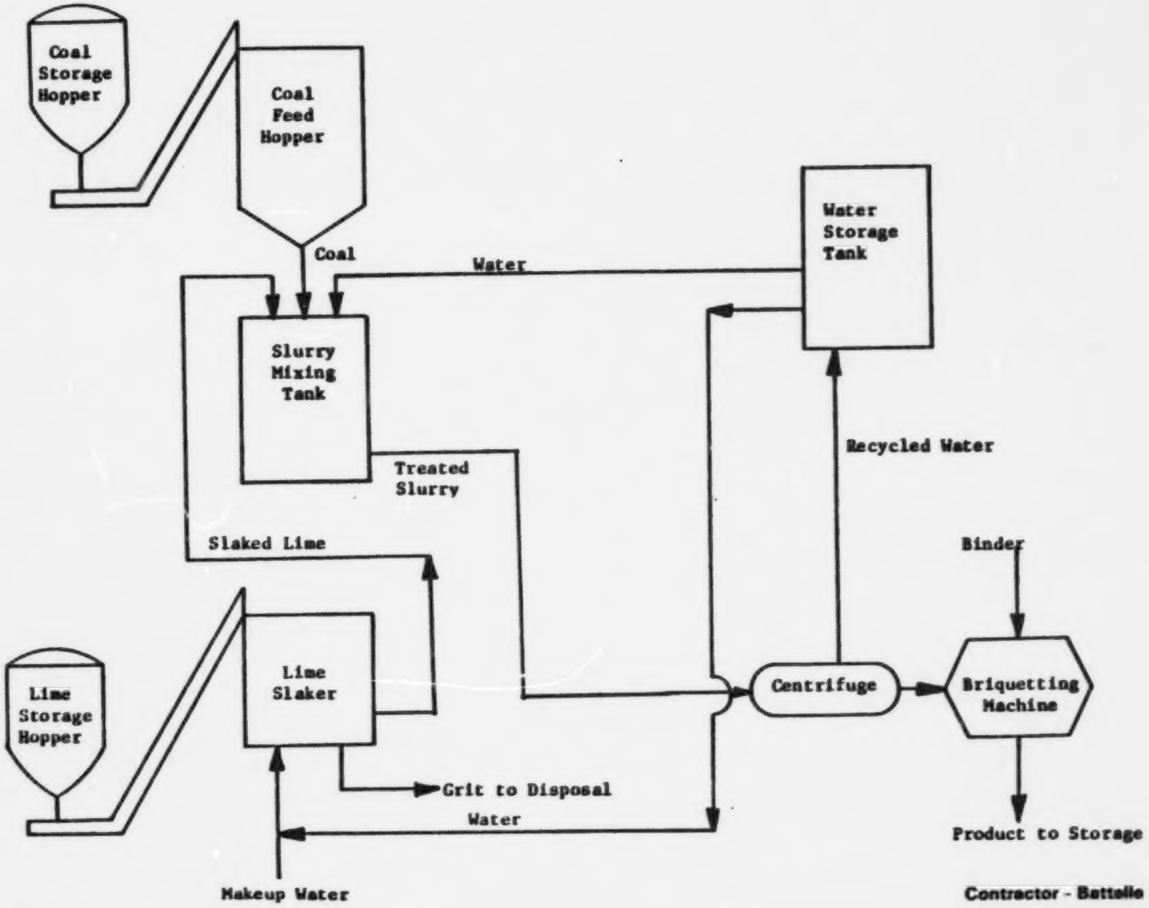
GASIFICATION OF UNTREATED COAL WITH H_2S REMOVAL


Flue Gas
Fuel Gas
Boiler
Steam
Calcium Treated Coal*
Gasifier
Cyclone
Boiler Feed Water
Air
Steam
Air
To Ash Disposal

* Supplied by off-site, central treatment facility.

GASIFICATION OF CALCIUM TREATED COAL

FIGURE 11. PROCESS VARIATIONS FOR FUEL GAS RETROFIT APPLICATIONS


Coal Storage Hopper
Coal Feed Hopper
Coal
Water
Water Storage Tank
Slurry Mixing Tank
Treated Slurry
Recycled Water
Slaked Lime
Binder
Lime Storage Hopper
Lime Slaker
Centrifuge
Briquetting Machine
Grit to Disposal
Water
Product to Storage
Makeup Water

Contractor - Battelle

FIGURE 12. PRODUCTION FACILITY FOR CALCIUM TREATED COAL

FIGURE 13. NOMINAL SULFUR CONTROL LEVELS CALCIUM TREATED COAL (LABORATORY SCREENING STUDIES)

	SULFUR REMOVAL, PERCENT	
	UNTREATED COAL	TREATED COAL
Moving-Bed Gasification	4[a]	80
Fluidized-Bed Gasification	[b]	85

Entrained Gasification	CONCENTRATION, PPM UNTREATED COAL	TREATED COAL
PRODUCT GAS		
H_2S	4500	370
HCN	33	10
SCRUBBER WATER FLASH GAS		
H_2S	5300	25
HCN	180	25
SO_2	8000	200

(a) Agglomeration occurred but gas flow through pellets allowed test to be completed.

(b) Test unsuccessful due to severe agglomeration of untreated coal in fluidized-bed gasification.

Contractor – Battelle

FIGURE 14. PROJECTED ECONOMICS FOR CONVERSION OF INDUSTRIAL GAS-FIRED BOILERS TO COAL

SYSTEMS	CAPITAL COST, $\$10^6$	OPERATING COST, $\$10^6$/YR	STEAM COST, $/1000 LB STEAM
Coal-Fired Boiler with FGD (Boiler and Scrubber New)	9.1	2.8	10.7
Gasification with FGD (Boiler Retrofit, New Scrubber)	9.8	3.1	11.6
Gasification with H_2S Removal (Boiler Retrofit)	10.4	3.1	11.9
Gasification of Calcium Treated Coal (Boiler Retrofit)	7.7	3.0	10.3

tail gases -

The reference control technology for the tail gases associated with acid gas stripping operations is direct incineration at approximately 1,600°F with a clean fuel gas. Alternative control methods which showed promise in a preliminary assessment study were incineration in a coal fired boiler at 4¢/MBtu (product gas basis) and catalytic incineration at 5¢/MBtu, while tail gas incineration with clean fuel gas is projected to cost in the neighborhood of 10-12¢/MBtu.[4] Commercial catalyst have been screened to determine the effect of temperature, space velocity, and the presence of H_2S and COS on hydrocarbon and carbon monoxide conversion (Figure 15).[5] These bench scale studies indicate the most effective catalysts are precious metal catalyst on a monolith substrate and a non-precious metal oxide deposited as micro spheres on a solid substrate (Figure 16). The more promising catalysts H, G, and A are currently undergoing life tests. A detailed analysis of the coal-fired incineration option is to be made by a commercial incinerator/ boiler manufacturer.

wastewater -

The control options for treating condensate wastewaters in a conventional mode have been demonstrated at bench scale. It appears that activated sludge is sufficient for coal wastewaters to meet existing discharge standards. Prior to biotreatment, gross ammonia and organic removal is required to render the feed non-toxic.[6]

Coal condensate waters contain dissolved ammonia, up to 2%. This NH_3 is usually neutralized by dissolved CO_2 that is produced in driving the conversion process; thus the condensate waters are strongly buffered and to change the pH via the addition of chemical reagents is normally quite expensive. Some coals contain high chloride which enters the condensate water and provides a strongly acidic anion to retain the NH_3 as NH_4Cl. In such instances, it is necessary to add a strong base (CaO) to enhance NH_3 strippability. Normally such coals occur in the East and the additional salt loading due to reagent addition presents no critical problem with effluent discharges.

Phenolic compounds contribute to the bulk of BOD (5,000-10,000 ppm) and along with other organics, pose a severe stress on sludge microorganisms. One typically resorts to solvent stripping and/or dilution to bring the levels down to 1000-2000 ppm, at which level acclimated organisms can do a reasonable job. An on-going study is determining the trade-offs between NH_3 and organic stripping options attempting to conserve reagents and at the same time, reduce steam requirements.[7]

Coal wastewaters contain some ring structures, polynuclear aromatics (PNA's) and heterocyclics (1-10 ppm), some of which are biorefractory. The more refractory compounds are adsorbed on the sludge, with effluent concentrations running in the range of 10-50 ppb. Laboratory bench testing has indicated that a significant reduction of PNA type materials can be achieved if the effluent is subjected to partial ozonation followed by activated carbon adsorption.[8] It appears important that the ozonation precede the sorption step, lest the large ring-structure compounds be too large for the pores of the carbon. Current efforts are focused at determining the efficacy of regeneration techniques for the spent carbon. Another study is attempting to demonstrate the viability of powder activated carbon (PAC) to help stabilize the biooxidation of solvent stripped condensate waters and improve the efficacy of activated sludge systems.[9] Biological screening tests are being performed on the various intermediate process waters to help ascertain the completeness of the treatment with regard to mitigating any low level adverse biological impact that may result by the release or use of partially

FIGURE 15. SUMMARY OF INCINERATION CATALYSTS TESTED

CODE	COMPOSITION	COMMENTS
A,F	*Spherical and Extrudate Forms, Non-Precious Metal Oxide on Support Material	Inexpensive, ~640 $\$/m^3$ Not Poisoned by Pb, Zn, Halides. <10 ppm SO_3 in Effluent. Used for CO, H/C and Other Organic Removal.
D	0.1% Pt, 5% Ni	"Some" SO_3 in Effluent. No Experience with Similar Streams. An NO_x Removal Catalyst Via NH_3 Reduction.
C	0.1% Pt, 3% Ni	Same as D, a Hydrogenation Catalyst
E	Pd on Metal Lessing Rings	<10 ppm SO_3 in Effluent. Expensive, ~1.4×10^5 $\$/m^3$. No Comment on Poisons. Can be Recycled 3 Times. Primarily Used for H_2 Removal.
H	Pt on Al_2O_3 Monolith Support	Favors SO_3 Production. Expensive, ~5.3×10^4 $\$/m^3$. No Comment on Poisons. For Industrial Tailgas Cleanup.
G	Precious Metal on Ceramic Honeycomb	~100 ppm SO_3 in Effluent. Expensive, ~6.4×10^4 $\$/m^3$. For Industrial Tailgas Cleanup.
B	Mn and Cu Oxides	Poisoned by S and Heavy Metals. Inexpensive ~710 $\$/m^3$. Designed Removal of H/C's and CO from Breathing Air.

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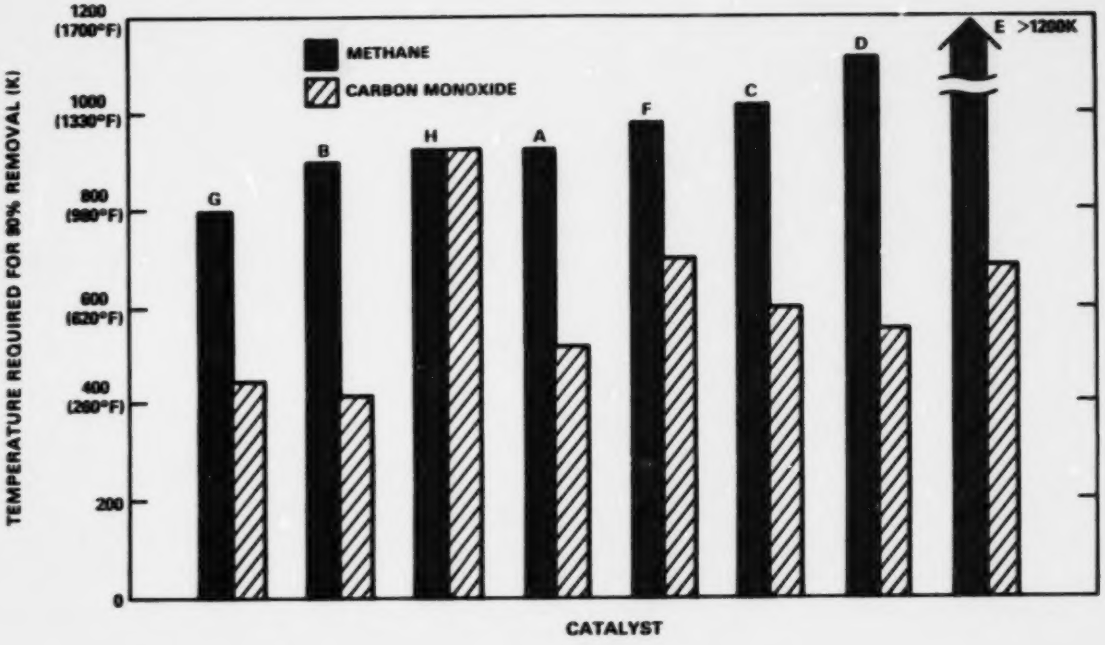


Note: ethane oxidation found comparable to methane, while catalysts tended to oxidize ethylene at lower temperatures, 600-800°K

FIGURE 16. METHANE AND CARBON MONOXIDE REMOVAL AS A FUNCTION OF CATALYST

Contractor — ORNL

treated effluents (Figure 17).[8] Note that the toxicity after biotreatment is suspected to result solely from inorganic species, i.e., the conversion of thiocyanates to ammonia during biotreatment (laboratory unit not as fully aerated as a commercial operation) and conversion of trace, residual cyanates to cyanide on ozonation. In some instances, a color problem has been associated with the aging of trace polyhydric phenols which may be overcome with a carbon polishing step or the addition of PAC to the activated sludge system. Unit operations can be arranged in a condensate treatment train that would produce almost drinking quality water. Relatively high treatment costs are likely to bar such intensive treatment (Figure 18); however, it should be noted that the cost impact under current standards is considerably less, expecially since only 10-20 gallons of condensate water may be produced per MBtu.[10] Costs also can be reduced if it is practical to resort to PAC in lieu of ozonation and activated carbon.

As indicated in the plant designs, the trend for wastewater control is to perform some partial treatment on the wastewater stream (solvent extraction, activated sludge) and use cooling towers to concentrate the stream to a point where a reasonably sized blowdown stream can be fed to evaporation ponds or multiple effect evaporators. Ideally it is economically desirable to use as poor a quality of water as the reuse application will permit. An on-going study is evaluating water quality requirements for a number of reuse applications, such as cooling towers, many of these applications have been previously outlined.[11]

Special attention has been given to reducing the quantity of wastewater associated with the quench operation by instituting a two stage quench - the initial stage is a low volume recycled highly contaminated water while the second stage consists of a much larger volume of relatively clean water, the strong acid gases condensing out in the first stage. The incentive for such a system has been shown to reside with coals having a halide content greater than 0.15% Cl, i.e., generally Eastern coals (Figure 19).[12] It is likely that future plant designs will adopt water conservation measures and desalting technology to preserve the water balance within the plant so that a concentrated, highly contaminated, low volume waste stream will be produced. Thermal oxidation techniques, e.g., gasification (recycle to the conversion process), wet-air oxidation, and even incineration, are expected to become viable treatment practice for the concentrate.

solid wastes -

As indicated, it is desirable to dispose of solid wastes in a manner tailored to the specific properties of the individual waste. Studies have been supported to classify major gasification and liquefaction slags/ashes as hazardous or non-hazardous under EPA/RCRA protocols (Figure 20).[13] It appears that such material may be disposed in a conventional manner, which can mean landfilling during mine restoration for strip mining operations near to the conversion facility. With the intent of better defining the true environmental acceptability of waste disposal practice for such materials, a series of laboratory column leaching and lysimetric tests are being performed to develop an understanding of leaching/mobilization phenomena and identify viable control procedures. Preliminary studies have shown high initial sulfur releases from gasifier slags and their auto-oxidation to sulfuric acid, may preclude the natural capacity of geologic material to adsorb migrating trace heavy metals. Incorporating an alkaline material (limestone, spent scrubber sludge, etc.) with the slag ash would tend to discourage acid formation during these critical, early leach cycles (Figure 21).

FIGURE 17. ACUTE TOXICITY TO DAPHNIA MAGNA OF HYDROCARBONIZATION WASTEWATER BEFORE AND AFTER VARIOUS TYPES OF WASTEWATER TREATMENT

SAMPLE	APPROXIMATE 48-HR LC_{50} (%)
Raw Scrubber Water	0.65
Biofeed Water	2.3
Biotreated Water	≈70
Water After Ozonation	≈18
Water After Ozonation and Charcoal Adsorption	≈0.1
Water After Charcoal Adsorption and Ozonation	≈4.5

Contractor — ORNL

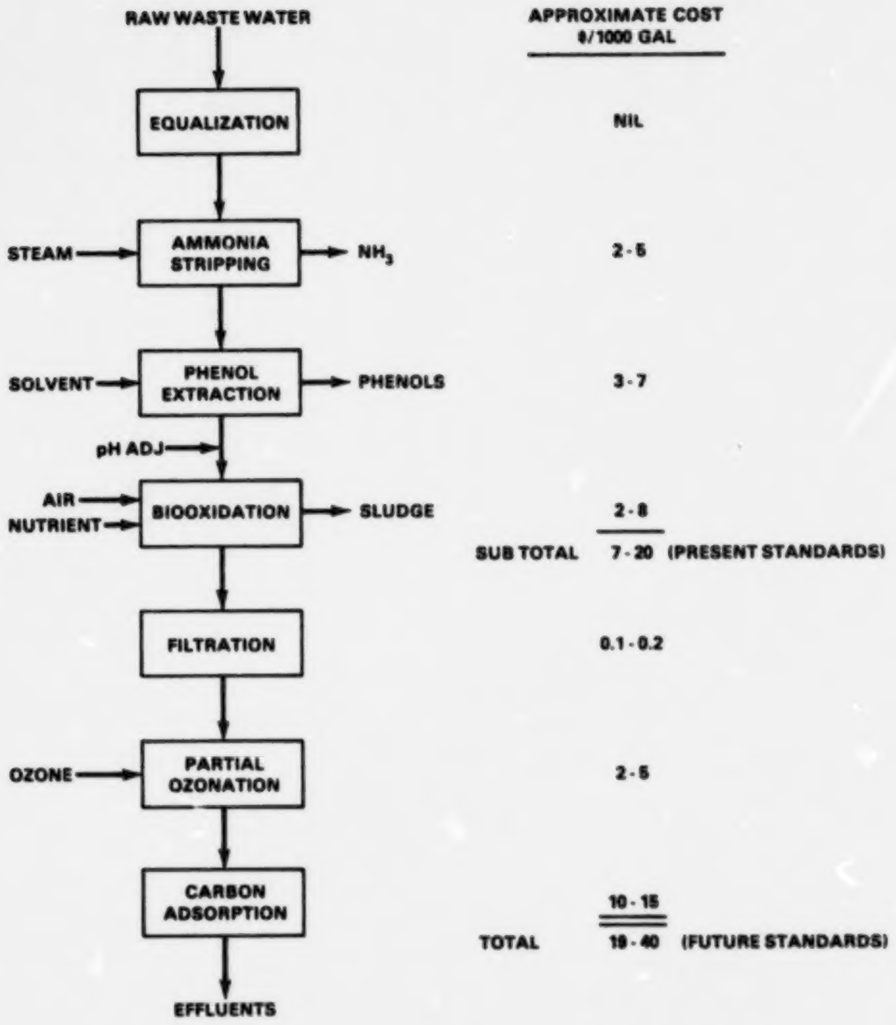
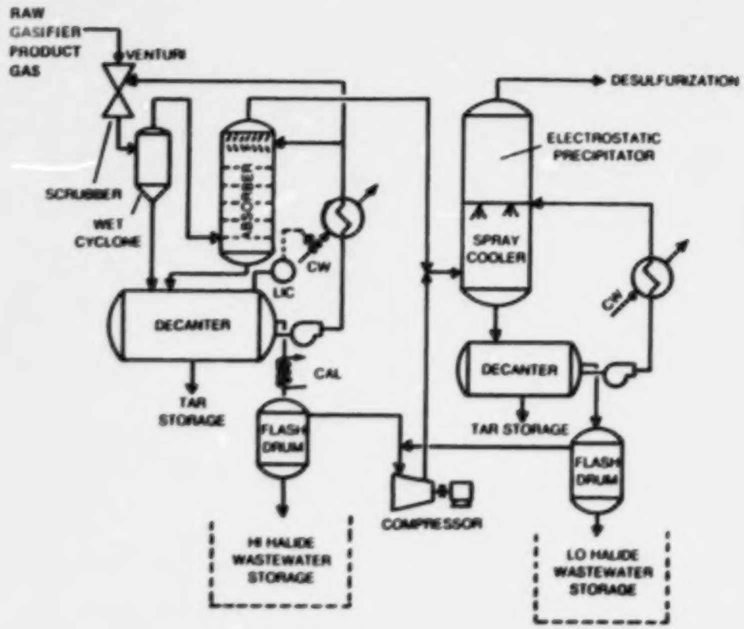
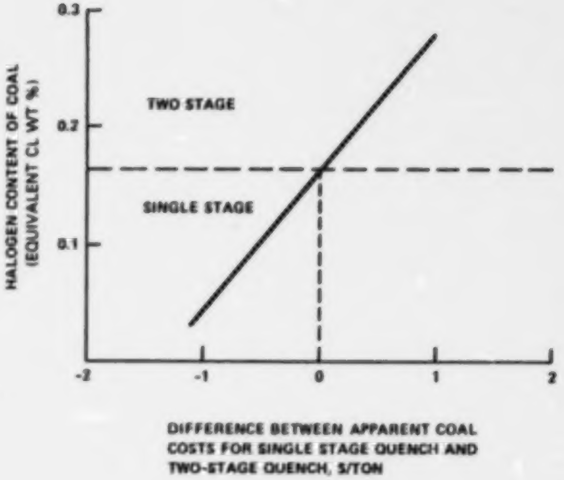

RAW WASTE WATER
EQUALIZATION
STEAM
AMMONIA STRIPPING
NH_3
SOLVENT
PHENOL EXTRACTION
PHENOLS
pH ADJ
AIR
NUTRIENT
BIOOXIDATION
SLUDGE
FILTRATION
OZONE
PARTIAL OZONATION
CARBON ADSORPTION
EFFLUENTS
APPROXIMATE COST
$/1000 GAL
NIL
2 - 5
3 - 7
2 - 8
SUB TOTAL
7 - 20
(PRESENT STANDARDS)
0.1 - 0.2
2 - 5
10 - 15
TOTAL
19 - 40
(FUTURE STANDARDS)

FIGURE 18. REPRESENTATIVE WASTE WATER TREATMENT PLAN FOR COAL CONVERSION EFFLUENTS

FIGURE 19. TWO STAGE QUENCH OPTION


RAW
GASIFIER
PRODUCT
GAS
VENTURI
SCRUBBER
WET
CYCLONE
ABSORBER
CW
LIC
DECANTER
CAL
TAR
STORAGE
FLASH
DRUM
HI HALIDE
WASTEWATER
STORAGE
COMPRESSOR
DESULFURIZATION
ELECTROSTATIC
PRECIPITATOR
SPRAY
COOLER
CW
DECANTER
TAR STORAGE
FLASH
DRUM
LO HALIDE
WASTEWATER
STORAGE



CONTRACTOR — ARTHUR G. McKEE

FIGURE 20. EPA-EP LEACHING RESULTS FOR SIX GASIFICATION/LIQUEFACTION SOLID WASTES[1]

ELEMENT	WASTE C	WASTE E	WASTE G	WASTE H	WASTE I	WASTE J	RCRA LIMITS[a]
		(All Concentrations in ppb)					
Arsenic	0.27	0.06	<1	<1	0.53	4	5,000
Barium	<200	<500	20	80	<500	3.3	100,000
Cadmium	0.064	0.97	<1	28	3.4	0.098	1,000
Chromium	1.6	0.44	<5	<5	0.13	0.46	5,000
Copper	2.7	3.7	10	10	0.94	1.3	b
Lead	<0.3	0.26	<10	<10	1.6	1.1	5,000
Mercury	0.64	0.03	<1	1	0.191	0.022	200
Selenium	<5	2	<1	<1	<1	<5	1,000
Silver	<0.03	<0.03	<2	<2	0.07	<0.01	5,000
Nickel	281	219	30	540	758	100	b
Zinc	63	10	13	2240	385	12	b

[a] RCRA Criteria are 100 times the interim primary drinking water standards.

[b] No criteria have been established for these elements at this time.

[1] Boegly, et al 1980. "Disposal Characteristics of Solid Residues from Coal Gasification." Air Pollution Control Association, June 1980, Annual Meeting, Montreal, Canada

Contractor — ORNL

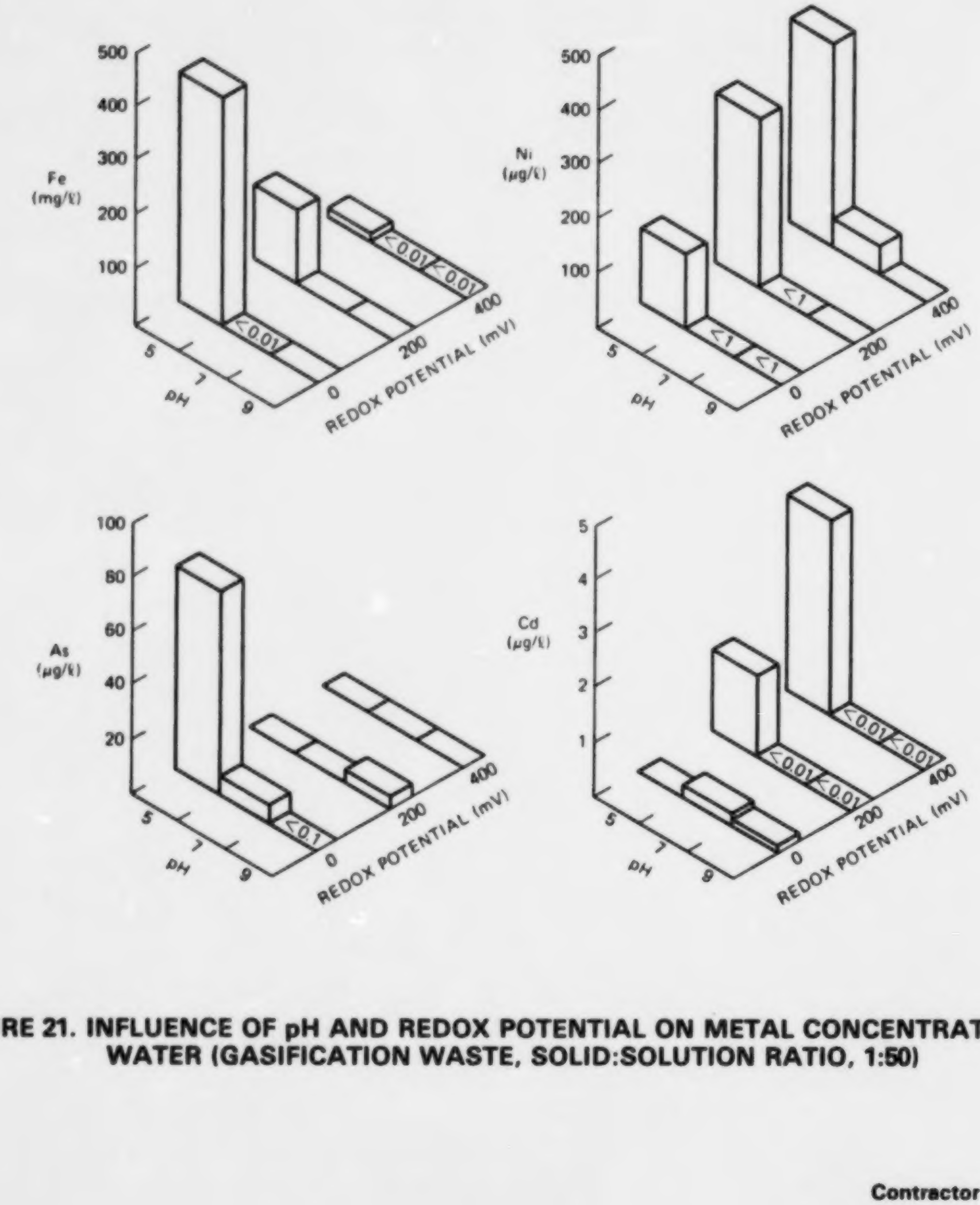


FIGURE 21. INFLUENCE OF pH AND REDOX POTENTIAL ON METAL CONCENTRATIONS IN WATER (GASIFICATION WASTE, SOLID:SOLUTION RATIO, 1:50)

Contractor — ORNL

CONCLUSION

Hopefully what has been conveyed by this broad-brush presentation is that a large number of environmental control options exist, that many of these control options are integrated into the process to improve the efficacy of the overall conversion process and lessen the concomitant environmental insults of the conversion process The inventory of viable control options are rapidly evolving: under such a dynamic situation where actual performance data on full-scale, environmentally acceptable facilities is lacking, it appears premature to develop firm BACT criteria. What would appear to be of greater service to the nascent industry would be a set of reasonable technology based emissions regulations or guidelines that would provide industry with the requisite freedom and flexibility and the incentive for innovation to operate within such bounds. In a nut shell, let's be prudent.

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TECHNICAL AND ENVIRONMENTAL ASPECTS OF THE GREAT PLAINS GASIFICATION PROJECT

Remarks of Gary N. Weinreich
Manager, Environmental and Community Affairs
American Natural Service Company

Ladies and gentlemen, it's a pleasure to have this opportunity to speak before you today about the Great Plains Coal Gasification Project. Unlike our presentations during the last seven years, today we can talk about a synthetic fuels facility that is under construction, a facility that will be the first commercial-sized substitute natural gas (SNG) plant in the United States, and a facility that represents a signal to the world that this country is serious in its efforts to reduce its dependency on foreign countries for its crucial energy supply. While this plant is by no means a panacea, it most definitely represents a major and difficult first step on the part of industry and government that will eventually lead to a successful new synthetic fuels industry in this country. Synthetic fuels, coupled with energy conservation and successful developmental efforts in the areas of solar power, non-conventional and renewable energy sources, will enable the United States to enter the twenty-first century in a much better energy supply and national security posture than is maintained today.

We must give a great deal of credit to the US Department of Energy for their assistance in the form of a federal loan guarantee for the project. With DOE's pledge of assistance, Great Plains was able to maintain the 1980 construction start date and avoid further delays in this long overdue venture. As you may be aware, the Federal Energy Regulatory Commission approved the Great Plains Project in November, 1979, but General Motors Corporation and three state commissions opposed the consumer-backed financing arrangements approved by the FERC. The federal loan guarantee alleviates this situation and has permitted the project to proceed. Ground was broken in August and construction of the facility will continue through to the completion date in 1984.

I was asked to speak on the technical and environmental considerations involved in a coal gasification facility such as the Great Plains Project. As you can imagine, this is a very broad subject to cover in 25 minutes. I will try to address the highlights and the bases for some of the environmental decisions involved in our project.

A brief organizational description of the Great Plains Project might be appropriate for those of you who are unfamiliar with the project. Great Plains Gasification Associates is a consortium made up of subsidiaries of five major natural gas pipeline companies. The project was originally proposed by ANG Coal Gasification Company, a subsidiary of American Natural Resources Company of Detroit, Michigan. ANG is now an equal partner in the project as well as the project administrator responsible for the design, construction and operation of the facility for the consortium. The other members of the consortium are subsidiaries of the Peoples Energy Company, Transcontinental Gas Pipe Line Corporation, Tenneco, Inc. and Columbia Gas Transmission Co.

The project consists of a 275-million cubic-foot per day high-BTU coal gasification plant which is being built in two half-size phases.

The project is located in Mercer County, North Dakota, six miles northwest of the town of Beulah (population approximately 3,000) and seven miles south of the plant's water supply, Lake Sakakawea. The plant is located immediately adjacent to an 880-megawatt steam electric generating plant currently being constructed by Basin Electric Power Cooperative of Bismarck, North Dakota. Together, the two plants will share common facilities such as water supply, railroad, plant access and coal mining. The power plant will supply electricity to the Great Plains facility while using the lignite fines which are unusable in the Lurgi gasifier. Together, the two plants complement each other and provide economic advantages while reducing the adverse environmental impacts of two separate plant sites.

The air pollution control systems included in the design of the Great Plains facility represent the largest single pollution control cost. The air emissions control system can be divided into four broad categories: 1) coal gasification, 2) steam generation, 3) coal handling, and 4) incinerators, flares and miscellaneous sources. Each category is unique and merits a brief explanation of the control alternatives.

The Great Plains' gasification system, like that of many other proposed SNG plants in the United States, will employ the Lurgi Rectisol process to remove acid gases from the synthesis gas stream. The Rectisol process uses a cold methanol wash to absorb CO_2, H_2S and other sulfur compounds from the product gas, and the methanol is then regenerated. Our engineers considered several options for treating the sulfur-containing off-gas streams from Rectisol. At first a Claus unit with tail-gas clean-up and a Wellman-Lord stack gas scrubber was considered. Detailed investigation, however, raised a number of questions about the operating reliability of the Claus system on a feed stream containing variable concentrations of H_2S. For this reason as well as high cost, a system utilizing the Stretford sulfur recovery process was selected for the Great Plains plant. The Stretford process is known to effectively reduce H_2S to less than 10ppmv; however, the Stretford process has not been proven on streams with as high a CO_2 content as that of the Rectisol off-gas.

For this reason, our plant includes a Stretford system designed to remove H_2S to a level less than 10ppmv, but our permit takes credit only for the vendor-guaranteed removal efficiency or 100ppmv. Of course, we are hopeful that the higher removal efficiency will be achieved and the plant-wide sulfur emission will be much lower.

The tail-gas from the Stretford unit will contain residual H_2S and virtually all the organic sulfur and hydrocarbons present in the feed from Rectisol. For this reason, incineration of the Stretford tail-gas is required. In the case of the Great Plains plant, this tail-gas will be incinerated in the plant boiler system, recovering the BTU value of the gas while converting the H_2S, organic sulfur and hydrocarbons to compounds acceptable for emission to the atmosphere. Although the Stretford tail-gas contains a very small BTU value on a cubic foot basis, it constitutes a major fuel source by virtue of its large volume. We, therefore, have found that combusting the Stretford tail-gas is preferable to flaring from an energy utilization, conservation and environmental standpoint. The environmental benefit results from increased energy efficiency which reduces the need to burn additional sulfur-containing fuel. In addition, with this boiler design, the gasification section of the Great Plains plant will comply fully with EPA's guidelines for the Control of Emissions from Lurgi Coal Gasification Plants (EPA-450/2-78-012).

This brings us to our second air emission source, the plant steam generation system. Several sources of steam generation are available to the designer of a modern SNG facility, including generation from coal fines or liquid by-products, recovery from exothermic processes (such as methane production), and recovery from gasifier steam jackets. The Great Plains plant will utilize plant byproduct tar, tar oil, naphtha, and phenols plus the Stretford tail-gas to generate the steam required above and beyond that recovered in an extensive in-plant steam recovery, reuse and conservation system. EPA's new source performance standards for steam generation apply to this section of the plant. However, the EPA emission standards are not suited to direct application in the case of Great Plains due to the innovative energy conservation approaches utilized. First, EPA has no sulfur emission standard for a sulfur-containing gaseous fuel such as the Stretford tail-gas. Further, EPA's NO_x emission standard does not consider NO_x emission from a liquid fuel (e.g. tar and tar oil) with a higher entrained nitrogen value than conventional liquid fuels. Fortunately, the North Dakota State Department of Health, from the time of our first project announcement, has been willing to evaluate our proposals in detail, carefully considering and balancing environmental, economic, energy conservation and safety criteria. After a thorough review with an invitation for public comments, the Health Department made determinations of 1) best available control technology for the project, 2) compliance with the federal guidelines for the Control of Emissions from Lurgi Coal Gasification Plants, 3) compliance with ambient air quality standards and 4) compliance with the Prevention of Significant Deterioration regulations at the Class I area 100 kilometers west of the plant site. The North Dakota State Department of Health, in their 167-page analysis of the Great Plains Project, found that the facility as proposed would comply with all federal, state and local air quality regulations. The EPA, Region VIII, then reviewed the state's analysis and congratulated the Health Department, stating that their technical effort "may well become the standard to which new source reviews of this office and the other Region VIII States are compared".

It is evident that in this case a very thorough evaluation of a new synthetic fuels facility was completed by means of a "case-by-case" review. The existence of new source performance standards, pollution control guidance documents or the like could very possibly have made permitting of the facility more difficult due to the inherent inflexibility of the regulations and the restrictions they impose when considering special situations and innovative techniques. A case in point is EPA's 1979 Environmental Assessment Report on Lurgi Coal Gasification Systems for SNG (EPA-600/7-79-120). This report contains an excellent overview of the environmental aspects of a Lurgi SNG facility. However, when applying the EPA guidelines and new source performance standards, the report incorrectly states that the Great Plains Project (refered to in the report as ANG) exceeds federal standards for SO_2 emission from the gasification section, exceeds the federal standards for SO_2 emissions from the steam and power generation section, and exceeds the federal standard for TSP emission from the steam and power generation section. This is after the Health Department and Region VIII certified that the facility is in 100% compliance with all regulations. The lesson to be learned is that hard-and-fast standards are not appropriate for complex emerging technologies such as those found in the synthetic fuels industry. A very thorough case-by-case review is highly preferable until such time as sufficient operating data on modern facilities have been compiled and verified and valid standards can be developed.

The other two sources of air emissions are 1) coal handling and 2) incinerators, flares and miscellaneous sources. Particulate emissions from the coal handling facilities will be controlled through the use of covered conveyors and baghouse collectors at all transfer points. EPA new source performance standards for Coal Preparation Plants applies to this section of the plant. The low-volume intermittent gaseous streams in the plant will be incinerated where such treatment is appropriate and does not represent a safety hazard. Start-up gases and expansion gases from gas-liquor separation will be routed to a start-up incinerator for controlled combustion. The majority of the coal lock-gas will be recovered, desulfurized and reused, resulting in a very small vent, less than 2% of the total lock gas volume. The flare system is the primary plant safety system and is capable of combusting the entire gas flow from either train of the plant in the event of an emergency shut-down of a gas processing unit.

The water pollution control systems included in the Great Plains Project are designed to eliminate the discharge of process wastewaters to surface streams. A complex recycle and reuse system will be employed within the plant followed by utilization of the plant cooling tower, multiple effect evaporators and a liquid incinerator to concentrate, then destroy all organic components of the plant wastewater. A brine solution from the regeneration of demineralizers and softeners will be disposed of via a deep well into an aquifer where the natural water quality is six times more brackish than the waste stream. Stormwater runoff will be collected in sedimentation ponds prior to discharge and the coal pile has been covered to minimize suspended particulate loading from that potential source. Sanitary wastewater will be treated in a package plant and the effluent will be discharged to the runoff pond which will provide tertiary treatment in the form of a polishing pond prior to discharge.

This system for handling liquid effluents was selected over other alternatives such as solar evaporation ponds, activated carbon adsorption and biological treatment after detailed engineering, economic and environmental review revealed that the present system is the best suited for our particular plant design and location.

Solid waste from the gasification plant consists primarily of coal ash from the gasifiers and from the liquid incinerator. Approximately 2200 tons per day of ash will be generated by the full plant.

This waste does not qualify as hazardous under the EPA's extraction procedure toxicity test and is further exempted as a coal combustion waste. Nonetheless, care will be taken in selecting and developing disposal areas within the mine. Disposal will be limited to dry locations where natural or emplaced clay barriers will prevent the formation and migration of ash leachates. In west-central North Dakota, the natural soil and groundwater conditions exhibit a relatively high pH and acid formed by the oxidation of pyrites is quickly buffered. Acid conditions and the resulting leachate problems evidenced in other parts of the country are not encountered in the Northern Great Plains region.

The in-mine disposal technique proposed to be used at the Great Plains Project represents a considerable improvement over the primary alternative which is ash sluice ponds. In-mine disposal eliminates four problem areas that occur with sluice ponds: 1) the commitment of large acreages for ponds, 2) the need to dispose of decanted water, 3) the need to reclaim the filled pond to a useful end-use and 4) the need to protect the groundwater from infiltration of sluice water. For these reasons, it is felt that proper in-mine disposal represents state-of-the-art in solid waste disposal.

In the area of employee health and safety, the Great Plains Project is designed to protect the worker from the potentially hazardous substances that are present in all synthetic fuels facilities. Containment of these substances and a good work practices control program coupled with a thorough medical surveillance program, are the essential elements of the occupational health and safety program. Our consulting agreements with the South African Coal Oil and Gas Corporation, Ltd. of South Africa enabled our engineers to discuss possible solutions to various air, water and process emissions and to select the most efficient means of control based on years of operating experience. As you may know, the Sasol plant was visited by an investigative team from the National Institute for Occupational Safety and Health (NIOSH) in 1977. The plant was given a clean bill of health by that group, a remarkable achievement for a facility that has been in operation for over 25 years.

In summary, we are confident that the Great Plains Coal Gasification Project can be built and operated in compliance with all requirements for environmental, health and safety control. In addition, our monitoring and surveillance programs will go beyond that required by regulation and will include data gathering programs necessary to develop a data base for future synthetic fuels projects. As always, we pledge our cooperation and assistance to the EPA and the other federal and state agencies wherever possible and we look forward to sharing the non-proprietary portions of our operating data so that sound substantiable regulations may be developed.

On behalf of the partners of the Great Plains Gasification Associates, I appreciate the opportunity to speak before you today and wish to extend an invitation to each of you to come to Beulah, North Dakota in 1984 and visit the first operating commercial-sized synthetic fuels plant in the United States.

Thank you.

Session II: ENVIRONMENTAL ASSESSMENT; DIRECT LIQUEFACTION

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Preliminary Results of the Fort Lewis SRC-II Source Test

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Introduction

The SRC pilot plant was designed to convert coal into a low sulfur and ash product in either solid or liquid form. The process that yields the solid product is called SRC-I, while the liquid product mode is referred to as SRC-II. This paper deals with the SRC-II operation.

The primary objective of this study is to evaluate environmental implications of the SRC-II technology on the basis of data obtained from the Fort Lewis SRC-II pilot plant. Efforts were made to sample and analyze non-site-specific streams that could be scalable to a full-size commercial plant. Although the characteristics of some of the streams collected may differ somewhat from their commercial counterparts, they may provide general qualitative information on pollutants expected from a commercial facility. Data obtained from this pilot plant must be carefully evaluated in order to determine their applicability and scalability to a commercial-size facility.

This paper first establishes basic similarities and differences in process and operation between the Fort Lewis SRC-II pilot plant and an expected commercial SRC-II facility. It then discusses an SRC-II sampling and analytical program being conducted by Hittman Associates, Inc. (HAI), and provides the data obtained thus far.

SRC-II Process Description

The SRC-II process involves non-catalytical treatment of coal with hydrogen at an elevated temperature (454°C) and pressure (13.8 MPa). In this process, a dried, pulverized coal is mixed with a process-produced recycle slurry to form a coal slurry. The coal slurry is then mixed with hydrogen and pumped through a preheater to a reactor where coal is dissolved and hydrocracked, liberating gases such as H_2S, H_2O, NH_3, CO_2, and hydrocarbons. The reactor effluent enters a series of pressure let-down vessels where process gases and liquid are separated. The gases are sent to an acid-gas absorber unit for the removal of H_2S and CO_2. The H_2S is further processed into a salable sulfur product. Light hydrocarbons and unconverted excess hydrogen leaving the absorber are cryogenically separated; the hydrogen gas is recycled to the process and the light hydrocarbons are processed into salable product gases. The light liquid stream is fractionated into naphtha and fuel oil. The product slurry is split into two streams. One of the streams is sent to the front end as recycle slurry to be mixed with feed coal, while the other stream passes to vacuum distillation where fuel oil is further recovered. The high-ash and low-sulfur residue (referred to as vacuum bottoms) from the vacuum distillation tower is sent to a gasifier for the production of make-up hydrogen or synthetic gas.

The Fort Lewis SRC-II pilot plant (Figure 1) does not have some of the process features described above. Many of the processes it employs are unique to the pilot plant and therefore would differ from those of an anticipated commercial facility. These differences are given in Table 1. Only if and when these differences are fully understood, can the data obtained be successfully extrapolated to the commercial operation to provide pollutant characterization and control technology information.

Sampling and Analysis Program

Background

HAI, under contract to the U.S. Environmental Protection Agency, began an SRC-II sampling and analysis effort in March 1978. The purpose of this effort was to evaluate the SRC wastewater treatment system and characterize the SRC-II products. Because of the important role of coal liquefaction to our nation's energy self-sufficiency and the environmental implications of this technology, this initial effort soon evolved into a comprehensive environmental assessment program to measure pollutants associated with the SRC-II operation. This program uses the EPA phased sampling and analytical approach to characterize emission and effluent streams from various processes and control units.

The first phase (Level 1) environmental assessment began in February 1979, and is now completed. Environmentally significant streams and their chemical components were identified, screened, and prioritized for more detailed second phase (Level 2) analysis. However, the SRC-II pilot plant underwent major system modifications and since then experienced start-up problems, which delayed the planned phase 2 sampling program. Meanwhile, the original SRC-II operation schedule was altered and the feedstock used (Powhatan No. 5) during the Level 1 sampling period was replaced with Powhatan No. 6. As a result of the process modifications and coal type change, the original Level 2 test plan was revised to include Level 1 and Level 2 sampling to be performed simultaneously to obtain the required sequential data. This combined Level 1/Level 2 sampling and analytical effort began in March 1980. Analyses of these samples are

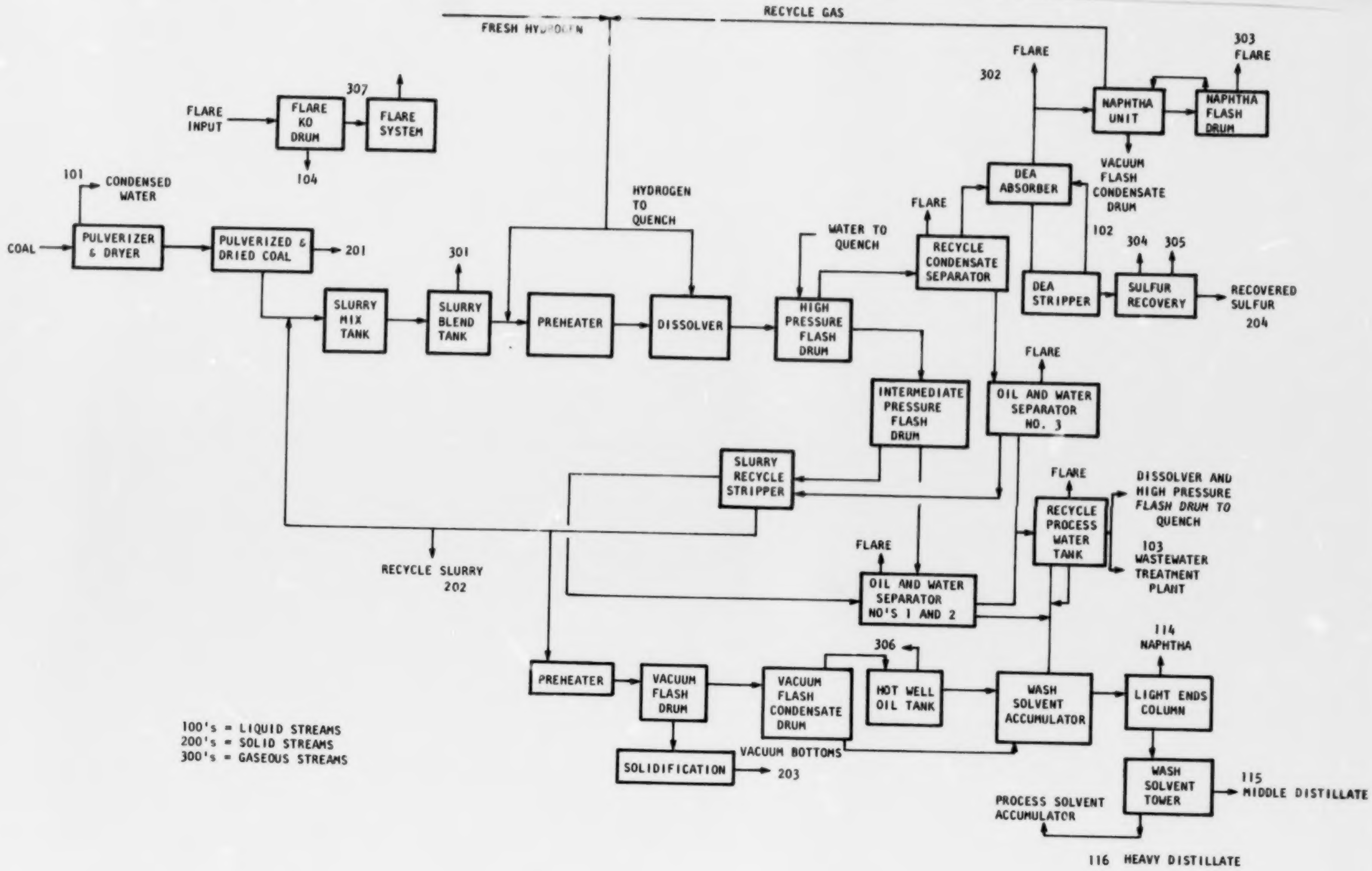

RECYCLE GAS
FRESH HYDROGEN
FLARE INPUT
FLARE KO DRUM
307
FLARE SYSTEM
104
101
CONDENSED WATER
COAL
PULVERIZER & DRYER
PULVERIZED & DRIED COAL
201
SLURRY MIX TANK
301
SLURRY BLEND TANK
HYDROGEN TO QUENCH
PREHEATER
DISSOLVER
WATER TO QUENCH
HIGH PRESSURE FLASH DRUM
FLARE
RECYCLE CONDENSATE SEPARATOR
FLARE
302
DEA ABSORBER
DEA STRIPPER
102
NAPHTHA UNIT
VACUUM FLASH CONDENSATE DRUM
303
FLARE
NAPHTHA FLASH DRUM
304
305
SULFUR RECOVERY
RECOVERED SULFUR
204
INTERMEDIATE PRESSURE FLASH DRUM
FLARE
OIL AND WATER SEPARATOR NO. 3
SLURRY RECYCLE STRIPPER
RECYCLE SLURRY
202
FLARE
OIL AND WATER SEPARATOR NO'S 1 AND 2
FLARE
RECYCLE PROCESS WATER TANK
DISSOLVER AND HIGH PRESSURE FLASH DRUM TO QUENCH
103
WASTEWATER TREATMENT PLANT
PREHEATER
VACUUM FLASH DRUM
SOLIDIFICATION
VACUUM BOTTOMS
203
VACUUM FLASH CONDENSATE DRUM
306
HOT WELL OIL TANK
WASH SOLVENT ACCUMULATOR
114
NAPHTHA
LIGHT ENDS COLUMN
WASH SOLVENT TOWER
115
MIDDLE DISTILLATE
PROCESS SOLVENT ACCUMULATOR
116 HEAVY DISTILLATE
100's = LIQUID STREAMS
200's = SOLID STREAMS
300's = GASEOUS STREAMS

Figure 1. Overall process flow diagram of the Fort Lewis SRC-II pilot plant.

TABLE 1. THE FORT LEWIS SRC-II PILOT PLANT Vs. COMMERCIAL SRC-II FACILITIES

Fort Lewis Facility	Commercial Facility	Affected Stream Characteristics
No gasification of Vacuum Bottoms. Vacuum Bottoms currently stored for outside disposal.	Vacuum Bottoms will be gasified, and resultant slag will be landfilled.	No emissions and waste discharge associated with Vacuum Bottoms solidification. However, in commercial practice slag and quenching water from gasification may pose disposal problem.
A portion of Sour Water is being recycled to provide a quenching stream.	Oil quenching is currently under consideration.	Alteration in process sour water characteristics expected.
Middle and Heavy Distillates produced separately.	Blended to yield fuel oil.	Will not affect overall pollutant balance. However, chemical constituents in the fuel oil may vary depending on the blend ratio.
Sour Water is not treated but diluted with non-process water prior to treatment.	Sour water will be pretreated to recover NH_3, H_2S, and phenols.	The pretreatment of sour water will affect the stream entering the wastewater treatment system. Consequently, different treatment process may have to be considered.
Fuel gases and purged hydrogen are being flared.	Fuel gases will be recovered. Cryogenic hydrogen separation obsoletes hydrogen purge.	Flare input stream is not representative of that of commercial facilities.
No hydrotreating of product fuels including Naphtha.	Products may have to be upgraded.	Lower heteroatomic compounds in the hydrotreated products.

still in progress. Preliminary data obtained from selected sampling streams are presented in this paper.

With the exception of analyses which called for non-composite sampling, such as volatile organic analysis, each aqueous or solid stream was sampled three times per day, 8 hours apart, for six sampling days, and was composited to constitute a single representative sample for a given stream. All aqueous samples were preserved according to EPA procedures, by organic extraction, or by refrigeration. Product streams were sampled once a day for six sampling days. In addition, a total of 36 samples were collected from four streams - wastewater treatment plant influent and effluent, and middle and heavy distillates - in order to perform a comprehensive statistical evaluation of process variability, sampling and analytical variability.

Gaseous streams were sampled once or twice per stream during the entire sampling period. Inorganic and organic species were collected in evacuated glass flasks, teflon bags, and Tenax GC and XAD-2 sorbent columns. Impinger bottles were used for species such as ammonia, cyanide, and volatile elements which could be collected and analyzed more effectively by wet-chemical or other methods. Collected volatile species such as H_2S, CO, COS, SO_2, and mercaptans were analyzed immediately using onsite GC columns equipped with species-specific detectors. Tenax GC columns were thermally desorbed and analyzed on a GC/MS system for the volatile species lost during extraction. Higher boiling organic compounds were extracted with methylene chloride in a Soxhlet extraction apparatus and subjected to GC/MS analysis. Table 2 presents the environmental source tests being performed on the collected SRC-II stream samples.

Table 3 shows metals present in dried coal (2 percent moisture) with their distribution among various products/by-products and their recycle process water (process sour water). As expected, most of the non-volatile metals present in the feed coal find their way into the vacuum bottoms. Use of the vacuum bottoms for a commercial gasifier will generate slag material which consists primarily of inorganic elements. Leaching characteristics of this material must be thoroughly investigated for the development of a safe method of disposal. This slag contains high levels of metals such as aluminum, iron, and titanium (see Table 3). The recovery of these elements may provide a potential disposal alternative. High levels of vanadium, sodium, iron, and other elements present in the elemental sulfur do not originate in the feed coal, but rather in the Stretford solution. Currently, the Fort Lewis plant produces unwashed sulfur which is transported for outside disposal. The

TABLE 2. SUMMARY OF TESTS TO BE PERFORMED ON THE SRC SAMPLES

STREAM NO.	STREAM IDENTIFICATION / ANALYSIS	Ammonia	Cyanide	Sulfide	COD	VOA	Metals	RCRA Leachate Analysis	Priority Pollutant Analysis	On-site Gas Analysis	Gas and Vapor Analysis (Organics trapped onto Tenax GC)	Vapor Analysis (Organics trapped onto XAD-2)	Level 1/Level 2 Organic Analysis	Level 1 Bioassay (Total Sample)	Level 2 Bioassay (Fractionated Sample)
101	Condensed water from coal dryer	●	●	●	●	●	●		●				●	●	●
102	Lean DEA Solution	●	●	●	●	●	●		●				●	●	●
103	Recycle Process water	●	●	●	●	●	●		●				●	●	●
104	Flare Knockout Condensate	●	●	●	●	●	●		●				●	●	
105	Solvent Fractionation Area Runoff	●	●	●	●	●	●		●				●	●	●
106	Dissolving and Separation Area Runoff	●	●	●	●	●	●		●				●		
107	Stretford Pad Runoff	●	●	●	●	●	●		●				●		
108	Feed Cooling Water	●	●	●	●	●	●		●				●		
109	Cooling Water	●	●	●	●	●	●		●				●		
110	Wastewater Treatment Plant Influent	●	●	●	●	●	●		●				●	●	●
111	Bio-unit Influent	●	●	●	●	●	●		●				●		
112	Bio-unit Effluent	●	●	●	●	●	●		●				●		
113	Sand Filter Effluent	●	●	●	●	●	●		●				●	●	●
114	Naphtha					●	●						●	●	●
115	Middle Distillate					●	●						●	●	●
116	Heavy Distillate						●						●	●	●
201	Pulverized & Dried Coal						●	●							
202	Recycle Slurry						●								
203	Vacuum Bottoms						●	●							
204	Elemental Sulfur						●	●							
205	Flottazur Skimmings						●	●					●	●	
206	Clarifier Sediment						●	●					●	●	
207	Digester Contents						●						●	●	
301	Slurry Blend Tank Vent						●			●	●	●	●		
302	Purge Hydrogen to Flare						●			●	●	●	●		
303	Light Hycrocarbons from Naptha Flash Drum to Flare						●			●	●	●	●		
304	Off Gas from Stretford Unit						●			●	●	●	●		
305	Stretford Oxidizer Tank Vent						●			●	●	●	●		
306	Hot Well Tank Vent						●			●	●	●	●		
307	Input Stream to Flare System						●			●	●	●	●		

TABLE 3. METALS PRESENT IN FEED COAL, PRODUCT/BY-PRODUCTS, AND PROCESS SOUR WATER

	Feed Coal (Pittsburgh Seam,) Powhatan #6	Vacuum Bottoms	Elemental Sulfur	Heavy Distillate	Middle Distillate	Naphtha	Process Sour Water
Aluminum	1.3%	2.8% (12%)**	1.4	7.7	<0.4	<0.4	<0.15
Antimony	<15	<15	0.3	<0.3	0.003*	2 x 10^{-4}*	5 x 10^{-4}*
Arsenic	11	23	<0.6	0.006*	0.004*	0.006*	0.007*
Barium	44	96	0.12	0.04	0.02	<0.002	0.008
Beryllium	< 0.3	<0.3	<0.006	<0.006	<0.006	<0.006	<0.003
Bismuth	-	-	<1.0	<1.0	1.0	<1.0	<0.5
Boron	-	-	<0.02	0.34	0.1	<0.04	230
Cadmium	2.5	<2.5	<0.05	<0.05	<0.05	<0.05	<0.025
Calcium	0.26%	0.53%	14.5	2.1	0.35	0.18	1.1
Chromium	18	52	0.3	11	0.39	<0.06	<0.03
Cobalt	3.1	7.6	<0.04	<0.04	<0.04	<0.04	<0.02
Copper	12	45	2.0	0.17	<0.03	0.18	0.015
Iron	2.3%	4.9% (21%)**	110	51	0.69	0.44	2.1
Lead	<0.1	<0.1	2.1	<0.16	<0.16	<0.16	<0.08
Magnesium	460	0.1%	0.7	0.35	0.35	0.08	0.08
Manganese	34	74	0.8	0.86	0.04	<0.006	0.03
Mercury	-	-	-	-	-	-	-
Molybdenum	5.8	17	0.8	0.77	<0.08	<0.08	<0.04
Nickel	12	35	0.4	4.1	<0.05	<0.05	<0.025
Phosphorus	310	660	1.2	<0.8	<0.8	<0.8	<0.13
Potassium	0.13	0.27	20	0.9	0.19	<0.02	0.4
Selenium	-	-	-	0.003	0.002	6 x 10^{-5}	3.4 x 10^{-4}
Silicon	-	-	2.5	3.7	1.75	2.3	3.4
Silver	-	-	<0.06	<0.06	<0.06	<0.06	<0.03
Sodium	410	730	0.1%	1.1	5.1	0.84	1.0
Strontium	69	150	0.1	0.05	<0.002	<0.002	0.004
Tin	<3	<3	<0.06	<0.06	<0.06	<0.06	<0.03
Titanium	630	0.14% (0.6%)**	0.1	0.35	<0.012	<0.012	<0.006
Tungsten	-	-	-	-	-	-	-
Uranium	-	-	-	-	-	-	-
Vanadium	34	77	34	0.07	<0.02	<0.02	<0.01
Zinc	13	39	4.0	0.1	0.03	0.35	0.03

*Determined by flameless AAS. All other elements were determined by ICP.
**Expected concentrations present in commercial gasifier slag.

Concentrations in µg/g, unless otherwise designated.

levels of metals found in the products are generally related to product volatility. Generally, levels of trace elements present in the heavy distillates are high when compared with either the middle distillate and naphtha. Heavy distillates are least volatile, middle distillates are next, and naphtha is most volatile. Process sour water contains low levels of metals, with the exception of boron. High pH and sulfide appear to be responsible for low metal concentrations in this stream.

Table 4 shows the reductions in various water quality parameters and trace elements from the wastewater treatment system. The wastewater treatment system is depicted in Figure 2. On the average, a 20 to 93 percent reduction in metals was accomplished by the treatment process. The table also shows trace elements found in the clarifier sediment and flottazur skimmings. Trace element analyses on RCRA extracts of these streams are currently being performed. Table 4 reveals that a high level of phosphorus is entering the treatment plant. The high level of phosphorus is attributed primarily to the blowdown from the cooling tower and boiler systems.

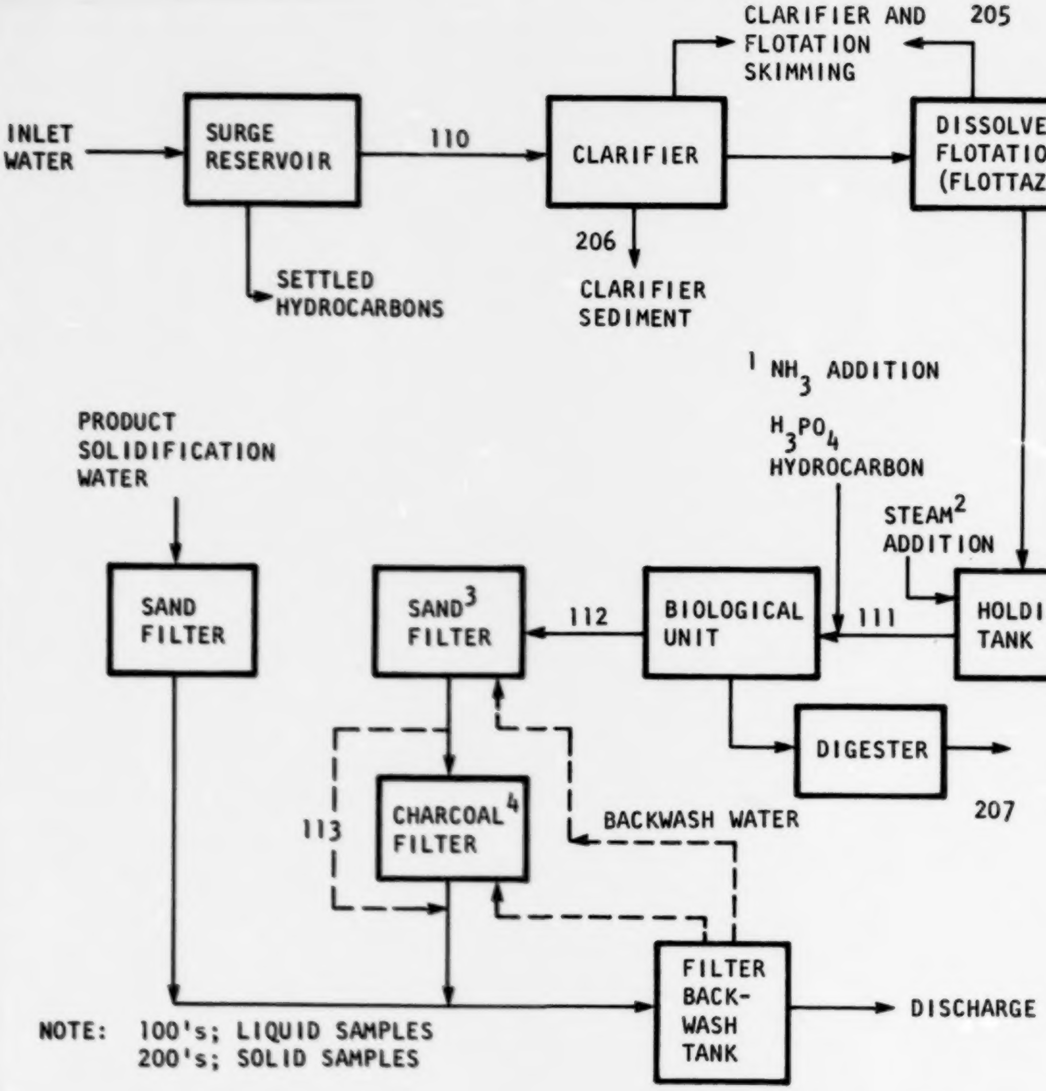
Figure 3 shows the effectiveness of this treatment in reducing organic class compounds. This figure, which was derived from the previous Level 1 data from the SRC-II operation with Powhatan No. 5 coal, indicates that the treatment system appears to be effective in lowering levels of organics such as aliphatic hydrocarbons, benzene and substituted benzenes, and fused polycyclic hydrocarbons. The effectiveness of the treatment system in reducing biological toxicity is shown in Figure 4. This figure was also derived from the previous Level 1 data. Neither the influent nor effluent demonstrated toxicity on the Ames or the rodent tests.

Analytical results of the SRC-II gaseous streams are shown in Table 5. While the slurry blend tank vent, the oxidizer tank vent, and the hotwell tank vent are emission streams discharged directly into the atmosphere, the Stretford offgas stream is sent to the flare system. Although the existing flare system receives emissions from the various pressure relief vessels, major input sources are the purged hydrogen, offgas from the Stretford unit, and light hydrocarbons from the naphtha scrubbing unit. Since fuel gases were not recovered but were being flared at this pilot plant, the characteristics of these flared gases would be quite different from those of a commercial facility. From an operational standpoint, the pilot plant flare unit is very similar to a commercial flare system operating under plant upset conditions.

TABLE 4. CHARACTERISTICS OF WASTE STREAMS FLOWING THROUGH THE WASTEWATER TREATMENT SYSTEM

	Influent	Sand Filter Effluent	Treatment Efficiency (%)	Primary Clarifier Sediment	Flottazur Skimmings
				mg/g dry base	
Ammonia	61	46	25		
Sulfide	5.1	0.4	92		
Cyanide	0.12	0.1	17		
COD	950	300	(68)	1770	1860
Aluminum	22	1.6	93	51	29
Antimony*	0.002	2×10^{-4}	90		
Arsenic*	0.03	0.006	80		
Barium	0.09	0.04	56	0.04	0.02
Boron	1.9	0.6	68	-	-
Calcium	19	15	21	5.7	3.3
Chromium	0.03	<0.03	-	0.12	0.07
Copper	0.2	0.04	80	0.4	0.2
Iron	45	8.5	81	72	44
Magnesium	5.4	4	26	1.1	0.7
Manganese	0.06	0.04	33	0.07	0.04
Nickel	0.025	0.025	-	0.06	0.04
Phosphorus	9.1	0.9	90		
Potassium	4	2.5	38	0.4	0.26
Selenium*	3×10^{-4}	2×10^{-4}	33		
Silicon	23	12	48		
Sodium	140	100	29	4.6	3.1
Strontium	0.11	0.07	36	0.06	0.04
Titanium	0.06	<0.006	>90	0.2	0.12
Vanadium	1.2	0.12	90	2.1	1.2
Zinc	0.9	0.1	89	1.8	1.1

*Determined by flameless AAS. All other elements were analyzed by ICP.


INLET WATER
SURGE RESERVOIR
SETTLED HYDROCARBONS
110
CLARIFIER
206
CLARIFIER SEDIMENT
CLARIFIER AND FLOTATION SKIMMING
205
DISSOLVED AIR FLOTATION UNIT (FLOTTAZURTM)
1 NH3 ADDITION
H3PO4
HYDROCARBON
STEAM2 ADDITION
HOLDING TANK
111
BIOLOGICAL UNIT
112
DIGESTER
207
PRODUCT SOLIDIFICATION WATER
SAND FILTER
SAND3 FILTER
CHARCOAL4 FILTER
113
BACKWASH WATER
FILTER BACK-WASH TANK
DISCHARGE

NOTE: 100's; LIQUID SAMPLES
200's; SOLID SAMPLES

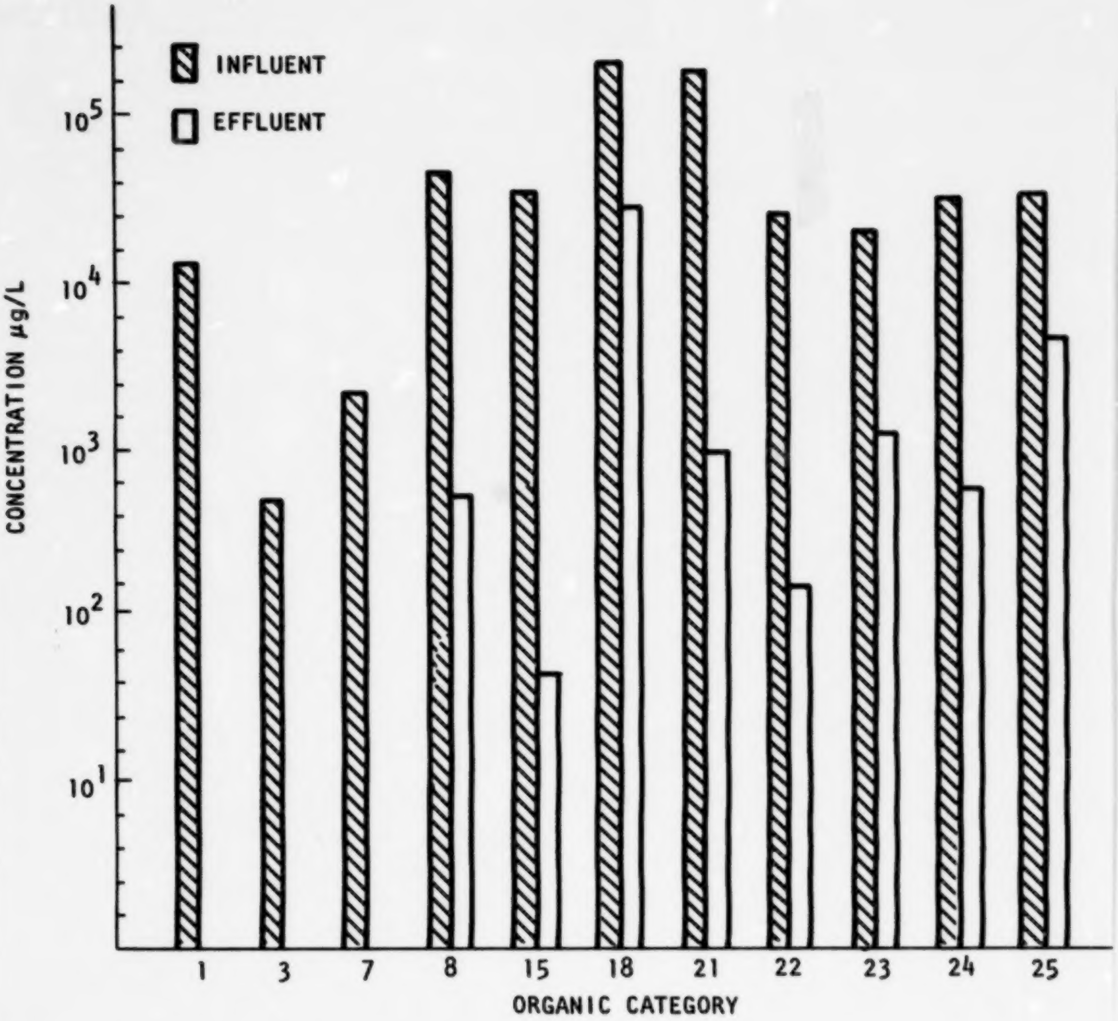
[1] WHEN WASTEWATER IS LOW IN NUTRIENTS DURING THE SRC PROCESS PLANT SHUTDOWN

[2] WHEN THE TEMPERATURE OF WASTEWATER IS LOW FOR NORMAL BACTERIA ACTIVITY

[3] THE SPENT BACKWASH WATER IS ROUTED TO THE SURGE RESERVOIR

[4] CHARCOAL FILTER WAS NOT IN USE DURING THIS SAMPLING

Figure 2. Overall flow schematic of the SRC pilot plant wastewater treatment system showing sampling points.



1 - ALIPHATIC HYDROCARBONS
3 - ETHERS
7 - ALDEHYDES, KETONES
8 - CARBOXYLIC ACIDS AND DERIVATIVES
15 - BENZENE AND SUBSTITUTED BENZENE HYDROCARBONS
18 - PHENOLS
21 - FUSED POLYCYCLIC HYDROCARBONS
22 - FUSED NON-ALTERNANT POLYCYCLIC HYDROCARBONS
23 - HETEROCYCLIC NITROGEN COMPOUNDS
24 - HETEROCYCLIC OXYGEN COMPOUNDS
25 - HETEROCYCLIC SULFUR COMPOUNDS

(Based on the average concentrations of three independently taken grab samples on February 11, 12, and 16, 1979, for the influent, and 2 independent grab samples taken on February 12 and 16, 1979, for the effluent).

Figure 3. Levels of organics present in the treatment plant influent and effluent.

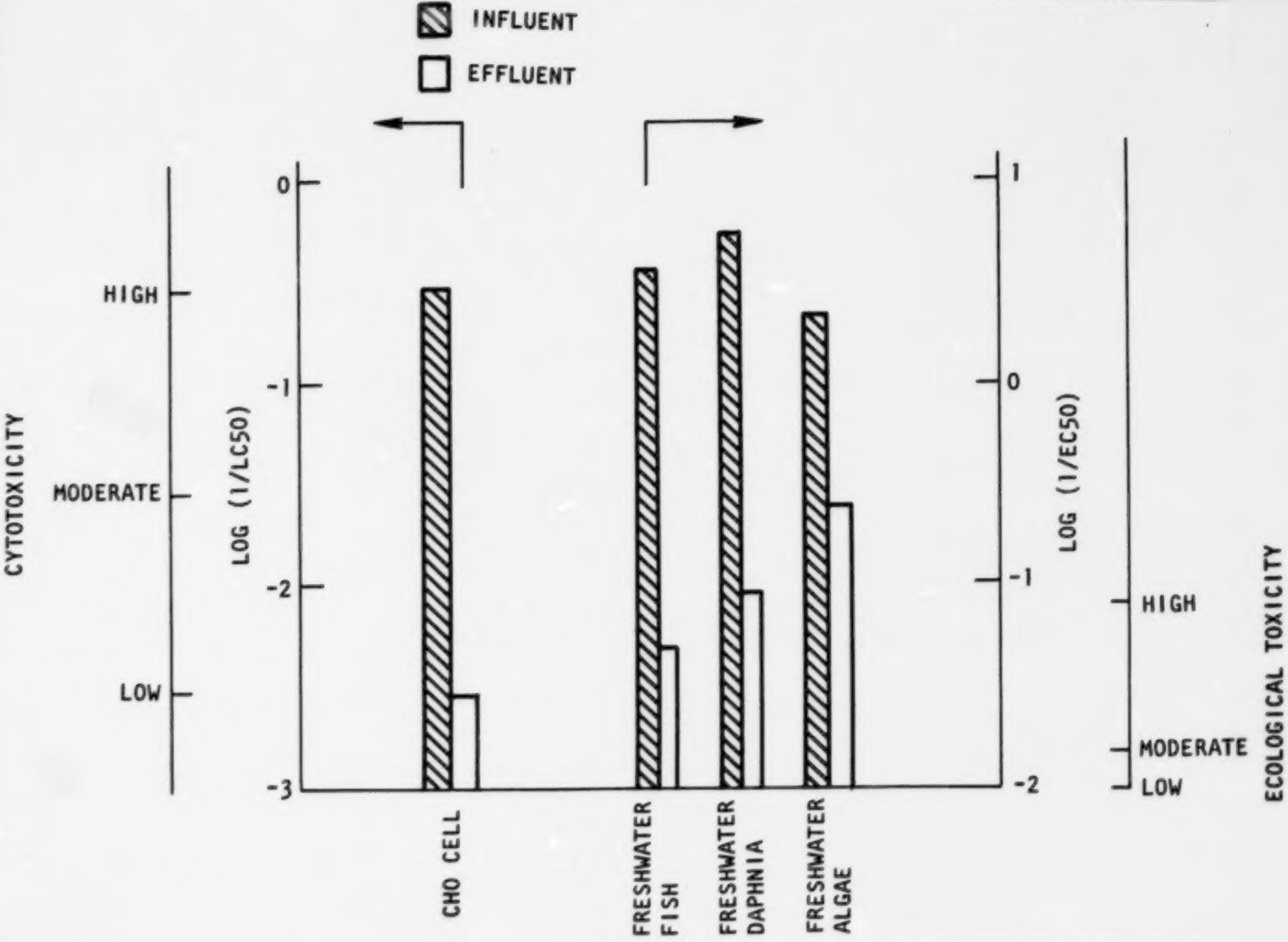


Figure 4. Reduction in biological toxicity by wastewater treatment.

TABLE 5. COMPOSITION OF THE SELECTED SRC-II GASEOUS STREAMS

Parameter	Slurry Blend Tank Vent (2-Day Average)	Stretford Offgas	Oxidizer Tank Vent	Hotwell Tank Vent	Input to Flare
C_1's	360	1.4×10^4	ND	2	1.8×10^4
C_2's	280	6,200	ND	290	2.9×10^4
C_3's	230	5,000	ND	50	3.6×10^4
C_4's	280	1,300	ND	50	1.3×10^4
C_5's	1,400	ND	ND	29	5,000
C_6's	1,400	ND	ND	12	3,000
H_2S	1,020	5,900	ND	ND	4.2×10^4
COS	3	40	ND	ND	40
Methyl Mercaptan	23	400	ND	ND	40
Ethyl Mercaptan	ND	40	ND	ND	220
Nos. of unidentified Sulfur Species	ND	3	ND	ND	3
CO	ND	2.5×10^4	ND	ND	5×10^4
NH_3	11	120	8	ND	88
HCN	ND	0.1	ND	ND	0.04
Species identified by GC/MS	phenol xylenes (O, M, & P-) Benzenes (C_2, C_3 & C_4-) benzofurans (methyl-) naphthalenes (C_1, C_2 & C_3-) phenanthrene/anthracene pyrene/fluoranthene	xylene benzenes (C_3 & C_4-) naphthalene (C_1, C_2-) tetralin phenanthrene/anthracenes (methyl-) pyrene/fluoranthenes (methyl-)	methyl benzofuran naphthalene (C_1, C_2, & C_3-) fluorenes (C_1 & C_2-) phenanthrene/anthracene (methyl-) pyrene/fluoranthene	benzene (C_3, C_4-) naphthalene (C_1, C_2, & C_3-) tetra/methyl benzofuran methyl teralin/ C_2-benzofuran	cyclopentene cyclohexanes phenols cresols xylenols xylenols benzenes (C_2, C_3 & C_4-) toluene furan xylenes (O, M, & P-) benzofuran naphthalenes (C_1, C_2, C_3, & C_4-) fluorenes (methyl-) phenanthrene/anthracene pyrene/fluoranthene tetralin

The Stretford offgas and the oxidizer tank vent are the Stretford process-related streams. The slurry-blend tank vent was designed to remove various fumes and vapors generated during the slurry/coal mixing. These pollutants are cooled and further condensed by a steam ejector prior to atmospheric release. Because sampling occurred at a point before the steam ejector, the information on pollutant characteristics shown in Table 5 is of limited value. For the hot well tank vent, the sampling probe was not placed in the vent duct, but rather, over the open end of the vent. Furthermore, the vent cycle could not be determined; thus, the concentration data shown in Table 5 provide only comparative quantitative information on the identified pollutant species. Table 5 shows the organic species identified by GC/MS. Compounds present in the streams did not vary greatly. Quantitative information on the identified species is not yet available, but is expected to be in the $\mu g/m^3$ range. It should be noted here that accurate sampling of high molecular weight compounds was difficult because samples could only be taken from existing sampling valves which were connected through a long, unheated sampling line to the main process streams. As a result, many high boiling organic compounds probably condensed out, and therefore, were not collected at the outlet.

For the selected liquid stream samples, volatile organic compounds were identified by GC/MS using the purge and trap technique (Table 6). Although the treatment plant influent contained volatile compounds which were collected from various sources, no detectable amounts of these compounds were present in the effluent. This probably resulted from atmospheric loss in the aeration unit rather than actual biological degradation of these substances.

Table 7 shows several important water quality parameters of the recycle process water. This stream was characterized by extremely high alkalinity with very low hardness and low levels of alkali metals. Actual COD for this stream should be somewhat higher than the value shown in the table. Volatile organic substances, including some phenolic compounds, were believed to be lost by purge gases (mostly H_2S) formed during acidification for sample preservation. The phenol level shown in the table was somewhat higher than expected (normally about 0.7 percent). Since a portion of this stream is recycled to the process, the phenol level at a given time is dependent on the recycle ratio, assuming that all other process conditions are constant.

TABLE 6. VOLATILE ORGANIC COMPOUNDS PRESENT IN THE SELECTED FORT LEWIS SRC-II STREAMS

	Recycle Process Water	Condensed Water From Coal Dryer	Solvent Fractionation Area (Fugitive Effluent)	Wastewater Treatment Plant Effluent	Sand Filter Effluent
Pyrroles	8.6 (4.2-16)		0.005 (0-0.03)	0.02 (0-0.1)	
Furans	0.3 (0-0.8)				
Pyridines	0.21 (0.05-0.3)	0.007 (0-35)		2.1 (0.04-3.7)	
C_4 Hydrocarbons	1.8 (0.4-4.2)		0.05 (0-0.08)	0.08 (0.02-0.2)	None Detected
C_5 Hydrocarbons	0.98 (0.2-1.4)		0.06 (0-0.1)	0.05 (0.02-0.1)	
C_6 Hydrocarbons	1.1 (0.5-2.0)			0.03 (0-0.06)	
Benzene	ND	0.21 (0.04-0.5)	0.21 (0.08-0.4)	0.06 (0-0.1)	
Ethyl Benzene	ND	0.3 (0-0.7)	0.26 (0.07-0.2)	0.06 (0-0.1)	
Toluene	11 (5-17.3)	0.33 (0.1-0.5)	1.3 (0.34-3.7)	0.24 (0.15-0.3)	
Xylene	0.64 (0-1.5)		0.13 (0-0.5)		
Unidentified - CN	8 (4.6-11.3)				
Chloroform				0.01 (0-0.06)	

NOTE: Concentrations in mg/L.
The numbers in parentheses represent the ranges of concentration variation over a 6-day sampling period.

ND = Not Detected

TABLE 7. CHARACTERISTICS OF RECYCLE PROCESS WATER (SIX-DAY AVERAGE)

pH	9.0
Alkalinity (as $CaCO_3$)	97,000 mg/L
Hardness (as $CaCO_3$)	10 mg/L
Ammonia (as N)	36,000 mg/L
Sulfide (as S)	30,000 mg/L
Cyanide (as CN)	1.3 mg/L
Chemical Oxygen Demand (as O_2)	26,000 mg/L
Phenol	7,600 mg/L
Cresols	2,850 mg/L
Xylenols & C_2 phenols	1,250 mg/L
C_3 Phenols	2,200 mg/L

Conclusions

More detailed analytical data and plant process information are still forthcoming. The results discussed herein are preliminary in nature, and require further confirmation and expansion as more data become available.

Most of the metals present in feed coal were almost entirely recovered in the vacuum bottoms. Use of this material for a commercial gasifier will generate slag, consisting almost entirely of inorganic elements. Detailed leaching characteristics must therefore be investigated in order to develop a safe method of disposal. The recycle process water contained mostly ammonia, sulfide, and phenols, and was essentially free of metals, except for boron. The boron level in this stream was over 200 mg/L. Because at levels exceeding 1 mg/L, boron has deleterious effects on the human body and the ecosystem, it may be necessary to remove it, along with ammonia, sulfide, and phenols, from this stream. In the coal drying process at the Fort Lewis pilot plant, moist air from the coal dryer is cooled with a dehumidifier and the condensed water is sent to wastewater treatment. This stream contains a number of pollutants of environmental significance. Although their levels are relatively low, these pollutants may have to be controlled since, in commercial facilities, the moist air resulting from coal drying is expected to be discharged as vapor into the air.

Due to several process upsets, the wastewater treatment samples may not fully reflect normal operating conditions.

ACKNOWLEDGMENTS

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CHEMICAL/BIOLOGICAL CHARACTERIZATION OF SRC-II PRODUCT AND BY-PRODUCTS

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ABSTRACT

Biological and chemical tests in concert with engineering analyses of plant operations have been used to provide data for the assessment of health and environmental effects of a mature coal liquefaction industry. In this report, we describe the methodology whereby biological testing is used to guide the chemist in the analysis of fractions of selected pilot plant materials. The principal components of an unmodified distillate blend from the SRC-II process are two-and three-ringed aromatic and heteroatomic species. Phenolic and polynuclear aromatic components are generally present at higher levels than expected in petroleum crudes. Biotesting, with the Ames test as the primary first tier method, revealed mutagenic activity. Chemical fractionation in conjunction with Ames testing implicates the primary aromatic amines as the compound class of primary concern. Chemical biotesting of a hydrotreated distillate blend showed a significant reduction of the primary aromatic amines as well as polynuclear aromatic hydrocarbons. Hydrotreating also can result in the reduction of sulfur- and oxygen-containing compounds, e.g., thiophenes and phenols.

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CHEMICAL/BIOLOGICAL CHARACTERIZATION OF SRC-II PRODUCT AND BY-PRODUCTS

Dependency of the United States upon foreign oil has led to the rapid implementation of programs oriented toward the development of new energy technologies. Simultaneously with the development of these synfuel processes, it is necessary to perform studies which will determine the potential health and environmental effects associated with the given technology. The purpose of this paper is to discuss the method and approaches used at the Pacific Northwest Laboratory in providing chemical and biological data dealing with SRC (Solvent Refined Coal) materials. The approach we have taken is designed to provide meaningful health effects data to the technology developers within the time frame which permits technology changes to be made optimally to ameliorate potential problem areas.

In evaluating the health effects associated with a coal conversion industry, it is essential that the chemist and biologist coordinate their research efforts toward a common goal. The usual scenario, however, results in the biologist asking the chemist to give him the compounds or materials with which he should be performing his assays. The chemist, on the other hand, asks the biologist which compounds are biologically active in order to orient his analyses toward these selected materials. The end result is usually one of utter frustration and mutual distrust leading to the confirmation as far as the chemist is concerned that the biologist doesn't really know what he is doing. The biologist, of course, already knew that about the chemist.

The problem is that the chemist is oriented toward the precise measurement of specific elements or compounds. Given a defined compound, a chemist, in many cases, can measure to femtogram levels. However, in the early stages of a developing technology such as coal liquefaction, the given compounds of concern have not yet been identified by the chemist nor has the biologist defined those materials which are biologically active. The chemist is thus faced with a horrendous task. He has in front of him what amounts to Beilstein's bucket of compounds and the effects with which the biologist is concerned may involve compounds whose toxicity or biological effects are so potent that miniscule quantities in this milieu of compounds may indeed be important. On the other hand, the engineer, who is concerned about the development of the process, usually doesn't give serious consideration to the problems of controlling his processes at micro levels. Yet, as we'll see in this paper, changes in the process will significantly affect the biological and chemical response of end products present at extremely low concentrations. The evaluation, therefore, of the biological impact of a given process requires effective coordination among the activities of the biologist, the chemist, and the engineer. In this paper, we will describe how this interaction has led to the definition of specific compounds of probable concern within the SRC process. Interaction with engineering personnel has led to the logical investigation of process parameters which may directly impact biological activity in coal liquefaction materials. One of the results of such interaction at Pacific Northwest Laboratory has been the identification of primary aromatic amines as compounds of principal concern. Hydrotreating, as will be seen, leads to a reduction of the biological activity of the SRC materials.

Chemical and biological characterization studies at the Pacific Northwest Laboratory have included GC, GC/MS, LC/MS analyses, specialized separations procedures for providing biological testing materials, microbial mutagenesis, in vitro mammalian cell toxicity and transformation assays, epidermal carcinogenesis (skin painting), acute and subchronic oral toxicity, developmental toxicity, dominant lethal assays, inhalation toxicity, and dosimetry and metabolism studies.

The approach to the study of SRC materials proceeds in basically three steps: in the first step, an engineering analysis defines the process and effluent streams in the pilot plant which are expected to be important in the final developed technology or to which there are expected to be high levels of occupational or populace exposure; in the second phase, materials selected in Phase 1 are subjected to biological screening tests and chemical characterization. Biological activity is usually detected using microbial assay systems. On evidence of activity, the material is chemically fractionated and the fractions subjected to bioassay. On the basis of the results of the microbial assay and the chemical characterization studies, materials are then selected for further study using mammalian cell cultures. The combination of results from cellular and microbial systems along with chemical characterization are then used to select materials which will be extensively analyzed by animal assays in the third phase. In this phase, materials are entered into animal systems for study of acute, subchronic, mutagenic and developmental effects. Certain long-term effect studies are also designed. Obviously, at each level of testing, other materials are employed including shale oil, petroleum crudes, other fossil-derived materials and pure known chemical mutagens and carcinogens for comparative purposes.

Material used in the studies described were obtained from the SRC pilot plant at Ft. Lewis, Washington. This pilot plant is operated by the Pittsburg and Midway Coal Mining Company for the Department of Energy. Materials from the pilot plant were selected on the basis of engineering design data for the projected demonstration plants of both the SRC-I and SRC-II processes. The selection of materials was based upon one or all of the following criteria:

a) The material is produced in significant quantity;

b) The material has potential for occupational and/or ecological enviornmental exposure;

c) The material can be obtained in a form which is considered by the best engineering estimates to be representative of demonstration or commercial level plant operations;

d) The material contains components which are already of known biological concern.

Consequently, the following process streams in the SRC pilot plant have been investigated: light oil, wash solvent and process solvent from the SRC-I process; and light, middle and heavy distillates from the SRC-II process. The boiling point ranges and specific gravity ranges for these materials are given in Table 1. The materials in all cases were obtained during equilibrium run conditions when the process was being operated for material balance determination. Given the conditions of pilot plant operations and pilot plant design objectives, these materials are probably not fully representative of materials expected from a commercial or demonstration plant.

However, the materials do provide information that may be of use in evaluating areas of toxocological concern whthin a given proposed process slate of products and effluents.

TABLE 1. Boiling Point Ranges of SRC Materials Used in Biological Experiments

Process	Material	Boiling Range (°F)	Density
SRC-I	Light oil	ambient to 380	0.72
	Wash solvent	380 to 480	0.96
	Process solvent	480 to 850	1.04
SRC-II	Light distillate	134 to 353	0.82
	Middle distillate	366 to 541	0.99
	Heavy distillate	570 to 850	1.10

CHEMICAL AND BIOLOGICAL STUDIES

The Ames mutagenesis assay provides a low cost method for the analysis of large numbers of samples in preliminary screening activities. In our laboratory, tests are carried out by mixing the test material with the Salmonella TA98 strain in the presence of mammalian liver microsomal enzymes (S9). By counting the number of revertants (from dependency on histidine in the media to nondependency on histidine) an index of mutagenicity induction is obtained for various test materials. As seen in Table 2, the heavy distillate and process solvent streams exhibit substantial mutagenic activity whereas the light oil, wash solvent, light distillate and middle distillate show no detectable activity.(1) By comparison, raw shale oil showed limited activity, and a crude petroleum (Prudhoe Bay) does not show activity in the Ames system.

To further define the response from the heavy distillate and process solvent materials, two fractionation procedures were employed: an acid-base scheme and a method based on LH20-Sephadex coupled with HP/LC. These schemes are diagrammed in Figures 1 and 2. While the acid-base sequence produces larger quantities of materials in a short period of time, the LH20-Sephadex method, when coupled with HP/LC, ultimately produces more refined cuts of

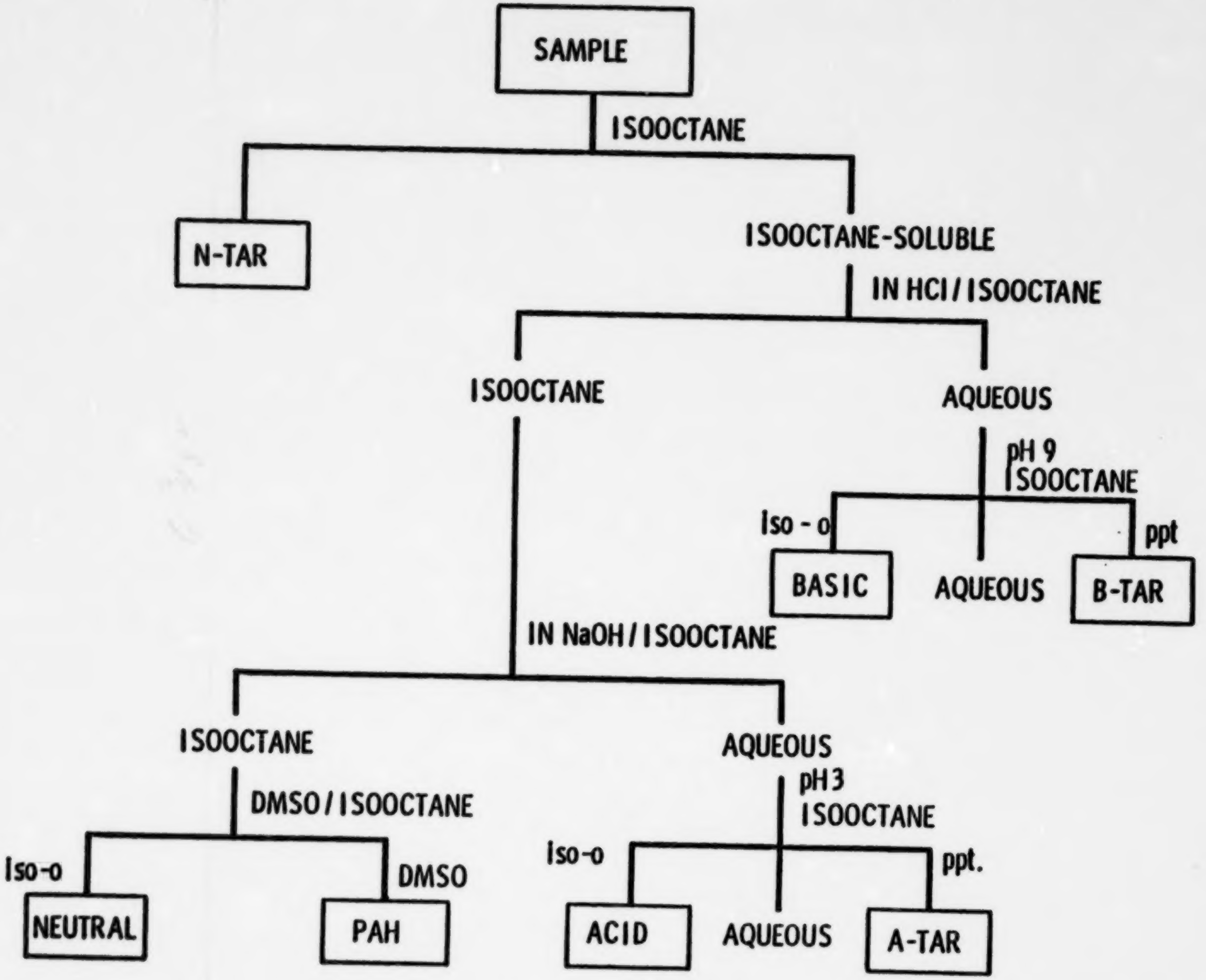
SAMPLE
ISOOCTANE
N-TAR
ISOOCTANE-SOLUBLE
IN HCl / ISOOCTANE
ISOOCTANE
AQUEOUS
pH 9
ISOOCTANE
Iso - o
BASIC
AQUEOUS
ppt
B-TAR
IN NaOH / ISOOCTANE
ISOOCTANE
DMSO / ISOOCTANE
Iso-o
NEUTRAL
DMSO
PAH
AQUEOUS
pH3
ISOOCTANE
Iso-o
ACID
AQUEOUS
ppt.
A-TAR

FIGURE 1. Acid-Base Fractionation Scheme

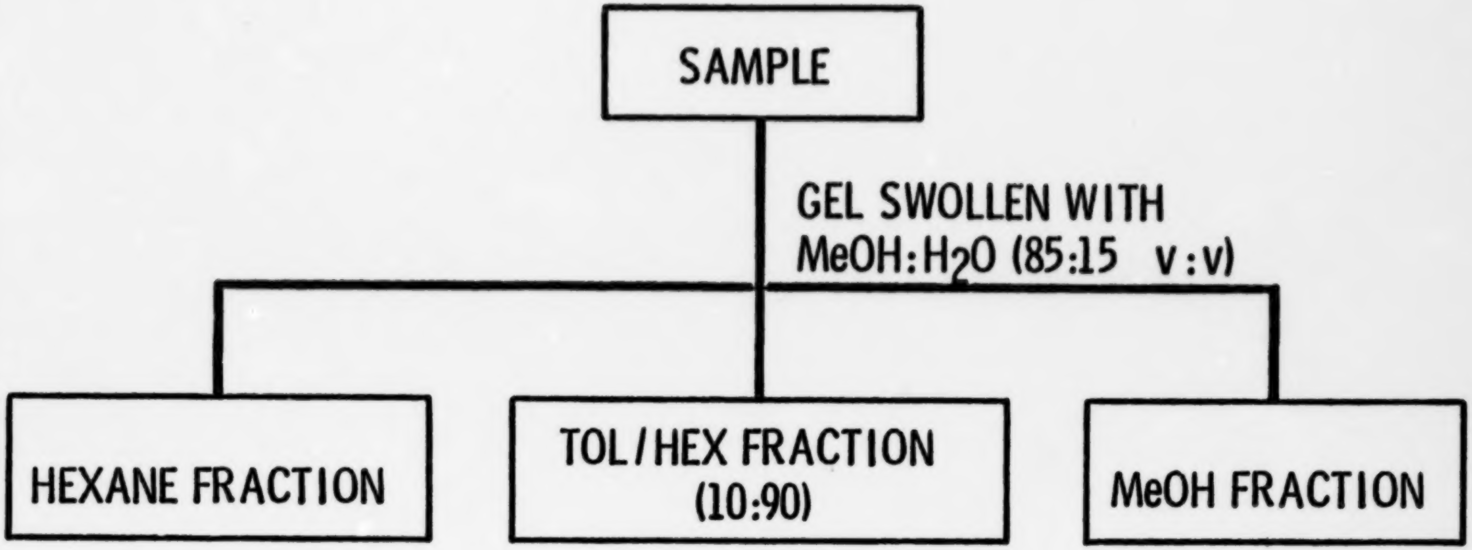
SAMPLE
GEL SWOLLEN WITH
MeOH:H2O (85:15 v:v)
HEXANE FRACTION
TOL/HEX FRACTION
(10:90)
MeOH FRACTION

FIGURE 2. Sephadex LH-20 Fractionation Scheme

material with less crossover among fractions. Fractions for biological testing are collected from HP/LC separations made on reverse phase NH_2 columns. Where minimal amounts of materials are required for biological testing, thin-layer chromatography has been effectively used to provide both separation and material for analysis. Acid and neutral fractions derived from HD by using the acid-base separation scheme showed relatively little response to the Ames test whereas the basic, basic tar and neutral tar fractions were mutagenically active.(2) The data for the basic and tar fractions yielded essentially linear dose-response data as seen in Table 3. While the specific activity was about one-half that of the basic fraction, the total mutagenic activity in the basic tar and neutral tar fractions was greater than that in the basic fraction because of the substantially greater mass of the tars. It is interesting that the neutral (non-tar) fraction which contains most of the PNAs exhibited little activity. This is probably due to the large number of compounds in this material which potentially prevent metabolic activation of the PNA components.

TABLE 2.(1) Comparison of the Mutagenicity of Solvent Refined Coal Materials, Shale Oils, and Crude Petroleums in Salmonella Typhimurium TA98

Materials	Revertants/µg of Material
SRC-I	
Process solvent	12.3 ± 1.9
Wash solvent	<0.01
Light oil	<0.01
SRC-II	
Heavy distillate	40.0 ± 23
Middle distillate	<0.01
Light distillate	<0.01
Shale Oil	
Paraho-16	0.60 ± 0.19
Paraho-504	0.59 ± 0.13
Livermore L01	0.65 ± 0.22
Crude Petroleum	
Prudhoe Bay	<0.01
Wilmington	<0.01
Pure Carcinogens	
Benzo(a)pyrene	114 ± 5
2-Aminoanthracene	5430 ± 394

TABLE 3.(2) Mutagenicity of Basic and Tar Fractions from SRC-II Heavy Distillate (HD)

Sample	a	b	ϕ
Basic fraction	198	7	1.00
Basic tar fraction	88	4	0.9
Neutral tar fraction	78	10	0.89

Controls

2-Aminoanthracene	14,000 rev/μg/μℓ DMSO
benzo(a)pyrene	406 rev/5 μg/5 μℓ DMSO
DMSO only	41 ± 15 rev/5 μℓ

Data for HD is in form $Y = ax + b$ in rev/μg where a is the slope, b is the interrupt, and ϕ is correlation coefficient, x is the amount of material in μg.

Analysis by TLC using a solvent system designed to preferentially separate the polar compounds from less polar constituents is presented in Figure 3 for the heavy distillate (HD) basic fraction. The TLC chromatograms were cut into strips, extracted with hexane/acetone mixtures and the extractant subjected to Ames assay using an S9 enzyme system. The activity associated with each of the separated fractions is shown in the section of Figure 3 designated S9. The chromatographic behavior of the materials shown here corresponds very closely to that expected for polar compounds such as aromatic amines. Similar results were obtained with the basic and neutral tar fractions of heavy distillate. High resolution mass spectrometry and GC/MS studies on the materials also indicated the presence of nitrogen containing compounds and, specifically, aromatic amines including aminonaphthalenes, aminoanthracenes, aminophenanthrene, aminopyrenes and aminochrysenes.

High resolution MS data also allowed a tentative identification based on elemental compositions for aminofluorenes and aminocarbazoles; confirmation of these assignments will require further work with adequate standards.(2) Isomers of the various amines were separable by capillary GC as

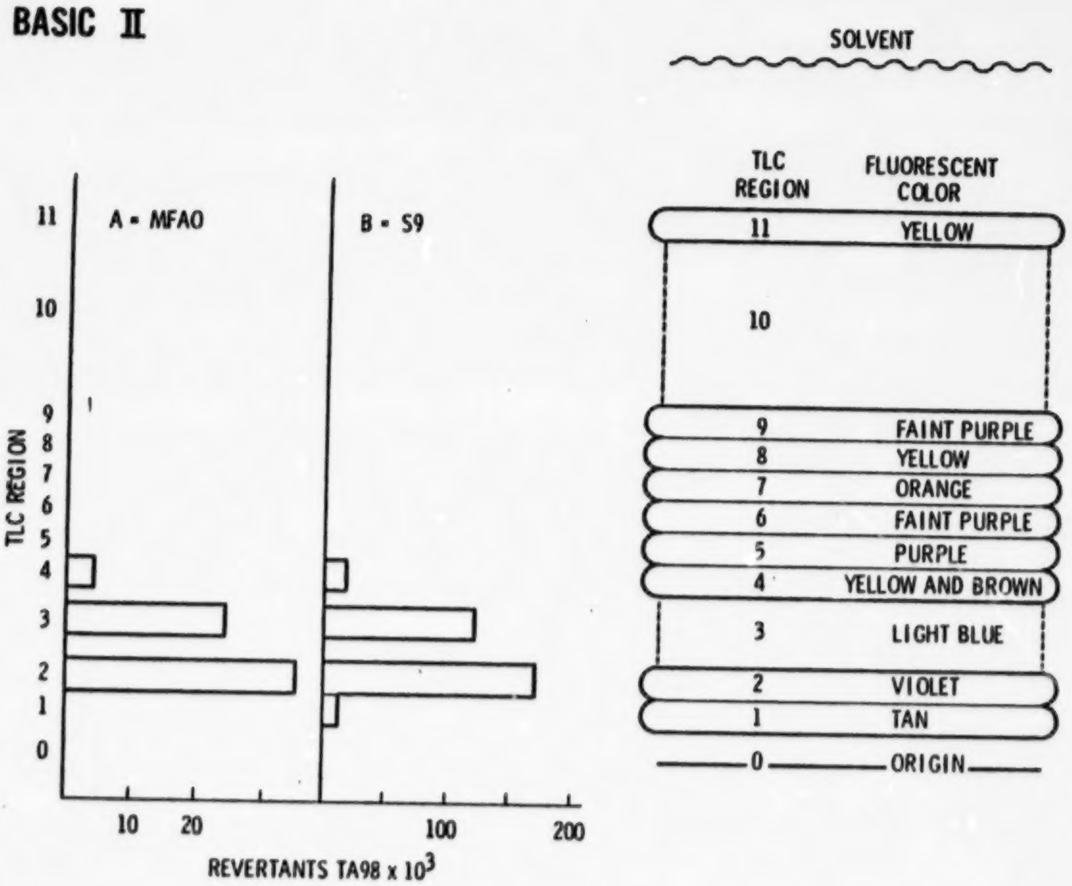

FIGURE 3. Ames Mutagenicity Analysis of Materials Eluted from Thin Layer Chromatogram of the Basic Fraction of SRC-II Heavy Distillate.

shown in Figure 4. Assignments specifically indicated in the figure were made on the basis of retention times of authentic standards.(2)

The correlation of the aromatic amine content with the biologically active regions from TLC of the heavy distillate basic fraction is shown in Figure 5. The relative concentrations of aminoanthracenes, aminophenanthrenes, aminopyrene and aminochrysene are seen to be highest in the regions with the strongest mutagenic activity. With the exception of aminonaphthalene, primary aromatic amines were not found in regions that lacked mutagenic activity. Aminofluorenes and aminocarbazoles have also been tentatively identified in the active regions. Analyses of these materials indicate that three and four ring primary aromatic amines are important mutagens, but that two ring aminonaphthalenes contribute little to mutagenic activity.

Since both GC/MS analyses and Ames results from the TLC fractions implicated the aromatic amines as the mutagenically active agents in the basic, basic tar, and neutral tar fractions of HD, a series of experiments were performed to further support this conclusion. One approach used the unique catalytic properties of mixed-function amine oxidase (MFAO), a purified liver enzyme system. This enzyme is specific for the matabolic transformation of primary aromatic amines to a mutagenically active state but is inactive with BaP and other polycyclic aromatic hydrocarbons. The 2-aminonaphthalenes are also not activated probably due to instability of the enzyme product. Mutagenic activity after activation of the HD basic fraction with S9 appears primarily in TLC regions with rf's of approximately 0.08 to 0.20. When activation was performed using MFAO, the same distribution of mutagenic activity among the TLC regions was found as with S9 as is seen by referring again to Figure 3 and comparing the MFAO with the S9. These results thus provide further evidence that aromatic amines are both present and capable of expressing their mutagenic activity in the basic fraction of HD.(1,3)

The above data were considered as presumptive for the involvement of the primary aromatic amines as causative agents in the mutagenic activity of the basic fraction and of the heavy distillate. Another more direct approach is also available to support this premise. Treating HD and its basic fraction with nitrous acid diazotizes aromatic amines and renders them nonmutagenic

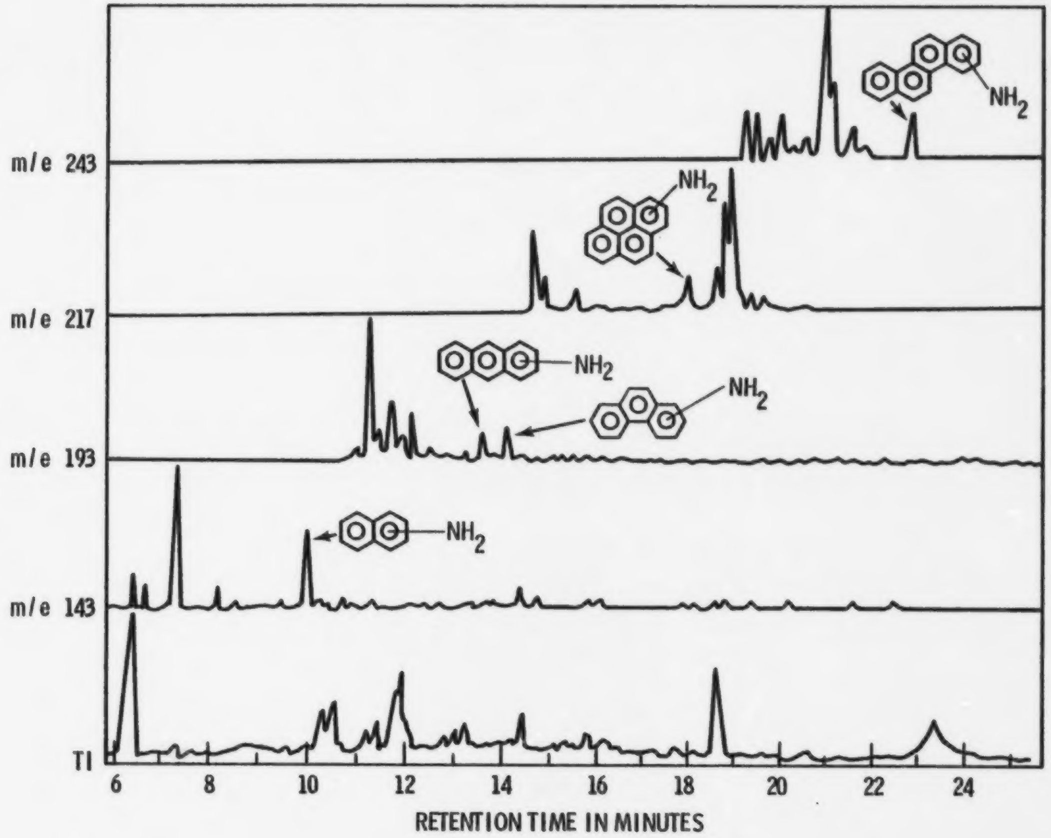

FIGURE 4. Single-ion chromatograms for the m/e 143 (M^+ for AN), the m/e 193 (M^+ for AA and APH), the m/e 217 (M^+ for AP) and m/e 243 (M^+ for AC) shown above the total ion current chromatogram of a mutagenic neutral tar subfraction of HD. Groups of peaks preceding the amino compounds arise from the methyl homologs of the corresponding nitrogen heterocyclic (e.g., methylacridine precedes aminoanthracene).

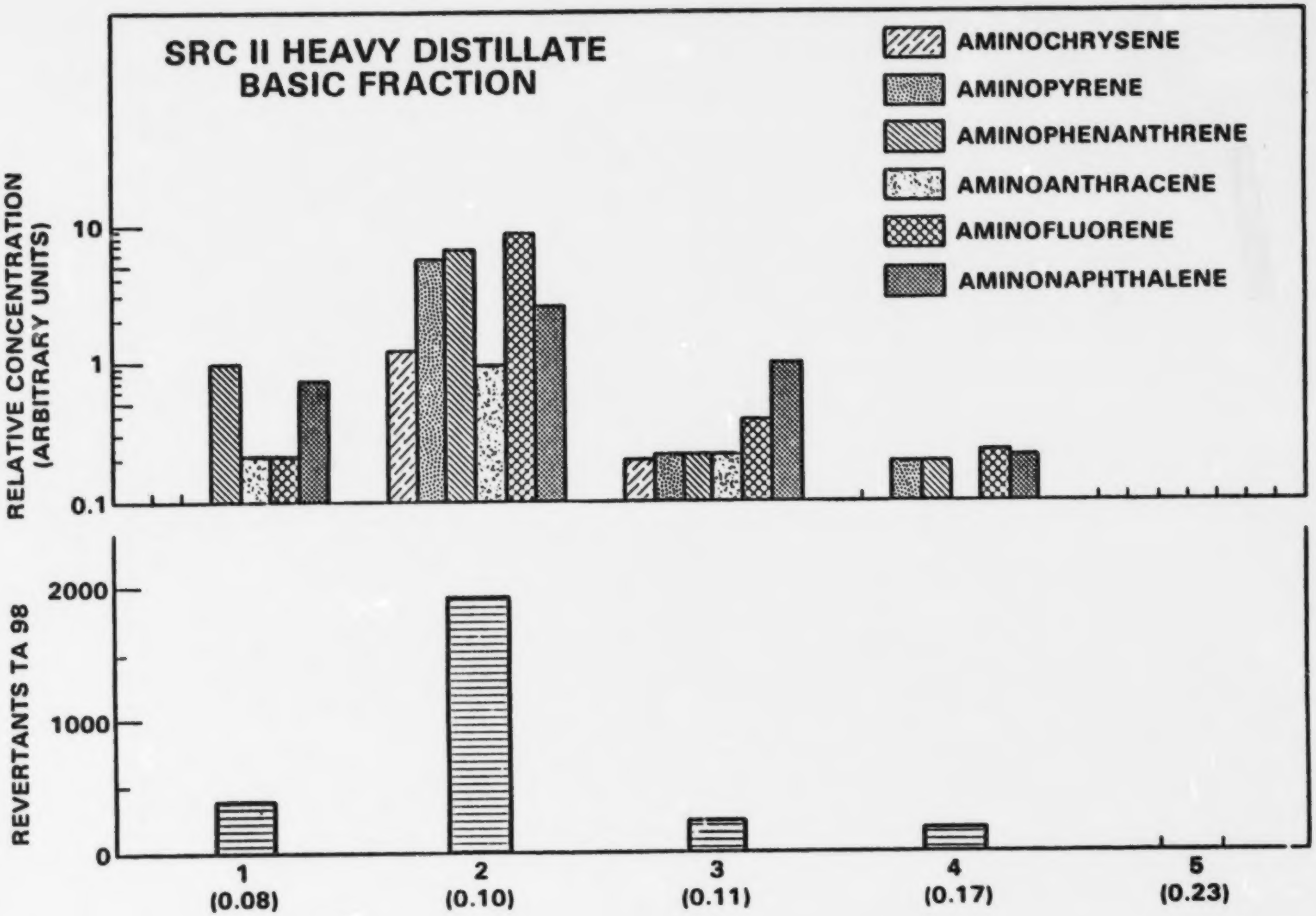

FIGURE 5. Identification and Relative Concentrations of Primary Aromatic Amines in Thin-Layer Chromatography Regions from SRC-II Heavy Distillate Cut, Basic Fraction

in the Ames system. Thus, disappearance of mutagenic activity in the basic fraction or in the heavy distillate after nitrous acid treatment would provide direct evidence for the mutagenic importance of this class of compounds. In Figure 6, it can be seen that the mutagenic activity of a pure aromatic amine 2-aminoanthracene is almost completely lost while the activity of benzo(a)pyrene or benzacridine is not affected by the nitrous acid treatment. Activity seen in heavy distillate, process solvent and their basic fractions is also mostly eliminated by nitrous acid treatment. As shown in Figure 6, activity of these materials after treatment with nitrous acid, is reduced to less than 10% of the original activity. It thus appears that much of the mutagenic activity is probably due to the presence of primary aromatic amines in both the crude material and in the basic fractions.(3)

HYDROTREATING

Since materials from coal liquefaction processes may at some point be used for chemical feedstocks or for further refining, it is possible that hydrotreating processes may eventually be employed in commercial SRC based plants. Hydrotreating, however, may also be expected to significantly impact nitrogen-containing compounds, particularly on deamination of the primary aromatic amines. Carbon-carbon bond cleavage will also occur which will also result in destruction of larger ring systems to form lighter weight alkylated and/or hydrogenated species. Loss of sulfur, nitrogen and oxygen in the form of H_2S, NH_3, and H_2O is also expected in heterocyclic compounds. Materials from the Ft. Lewis pilot plant which had been subjected to hydrotreatment were therefore examined.

While the hydrotreated samples were generated under process conditions which represent current commercial practice, final demonstration scale designs are not yet available. Thus the results of the hydrotreatment processing can be evaluated only in general terms.

Material obtained from tankage accumulated over a series of pilot plant runs extending from October 1978 into the early part of 1979 was subjected to hydrotreating by Universal Oil Products. A middle distillate to heavy distillate blend ratio 2.9 to 1.0 was determined from the average yield ratios of runs during this period. Obviously because of the long-term

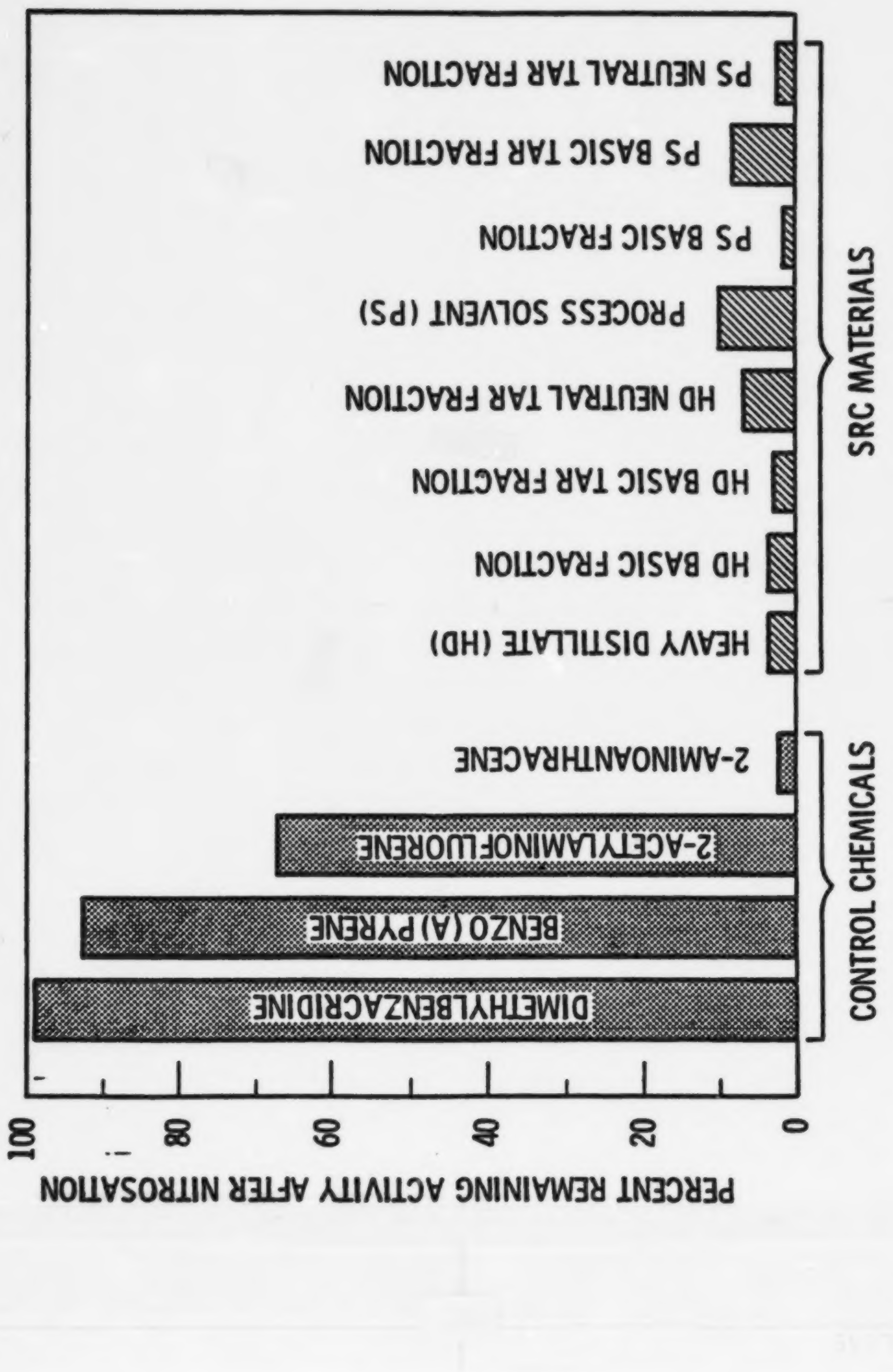

FIGURE 6. Effect of Nitrosation on Mutagenicity of SRC Materials

accumulation period, there are some difficulties in assessing sample representativeness and processing history due to the numerous modes ranging from steady state to upset conditions of operation and to the unavoidable product variability from one run to another. Materials were hydrotreated in standard research fixed bed reactors using a commercial UPO catalyst. Analysis of the materials of the distillate plant before and after hydrotreatment showed dramatic differences in gross chemical composition. GC/MS runs were made with SE2250 or SE52 coated capillary columns. Examples are given in Figure 7. The reconstructed total ion chromatograms of the materials show that there is a dramatic reduction of multiring compounds and phenols with subsequent conversion into hydroaromatic materials, specifically tetralins and their alkylated homologs. Table 4 summarizes the GC and GC/MS data and gives the concentrations in ppm for various compound classes before and after hydrotreatment. Severe hydrotreatment resulted in the reduction of total phenols from 130 ppm to 17 ppm in the total distillate blend. Aromatics and N-heterocyclic compounds show significant reduction. Introduction of hydrogen to the rings is obviously demonstrated by the appearance of compounds such as tetrahydroquinoline, tetrahydrocarbazole and tetrahydrozapyrene, tetralins and other hydrogenated multiring compounds. Primary aromatic amines, initially present at a total concentration of 1.9 ppm, are below the detectable range of GC and GC/MS following hydrogenation under the conditions employed. Figure 8 gives a graphic summary of the results for the compound classes affected.

Biological activity associated with the basic, base-induced tar, acid-induced tar and isooctane-induced tar fractions of the distillate blend followed the trend shown by chemical characterization in loss of the primary aromatic amines (Figure 9). Moderate hydrotreatment, for example, reduced the mutagenic activity of the basic fraction from 16.2 to 2.2 revertants per microgram (Table 5). This is a reduction in the weighted contribution to total mutagenicity from .86 to .03 revertants per microgram feedstock. The tar fractions were reduced in potency to levels below the limits of detection. While the specific effects of hydrotreatment upon chemical composition and biological activity of a given coal-derived fuel product will depend upon reaction conditions, catalysts, and starting material composition, it nonetheless appears that hydrotreatment will, in general, result in products with reduced mutagenic activity. This is probably due to the reduction of

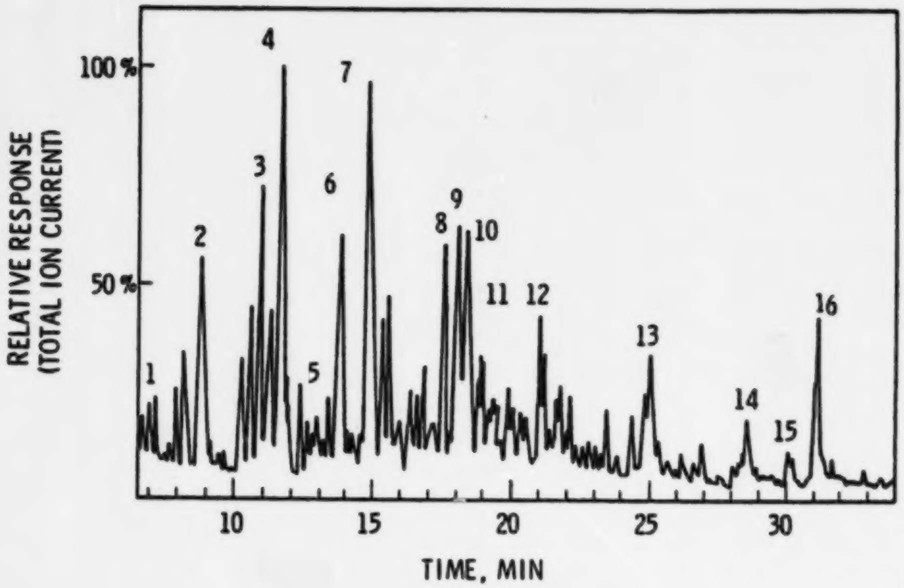

FIGURE 7a. Reconstructed Total Ion Chromatogram of SRC-II Distillate Blend(4)

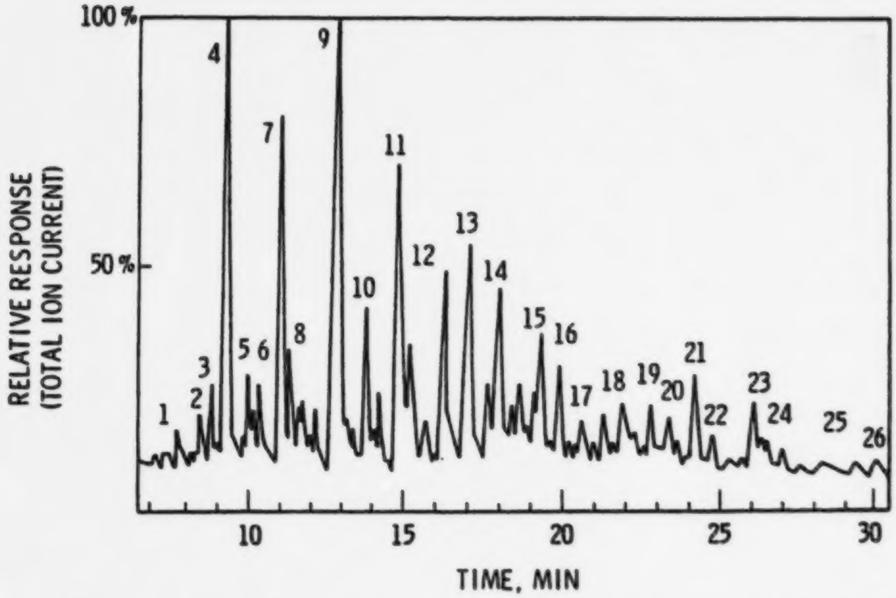

FIGURE 7b. Reconstructed Total Ion Chromatogram of Severely Hydrotreated SRC-II Distillate Blend(4)

See legend next page

(See legend on page 158)

LEGEND TO FIGURE 7

Reconstructed total ion chromatograms comparing unfractionated SRC-II feedstock, Figure 7a, with the severely hydrotreated material, Figure 7b. Principal peaks are identified in both chromatograms: (a) 1: phenol, 2: C_1 phenol, 3: tetralin, 4: naphthalene, 5: indole, 6: C_3 phenol, 7: C_1 naphthalene, 8: biphenyl, 9: C_2 naphthalene, 10: phenylether, 11: dibenzofuran, 12: acenaphthene, 13: fluorene, 14: C_1 fluorene, 15: dibenzothiophene, 16: phenanthrene. (b) 1: methyldecalin, 2: methylindan, 3: methyltetralin, 4: tetralin, 5: dimethylindan, 6: dimethylindan, 7: methyltetralin, 8: dimethylindan, 9: methyltetralin, 10: ethyltetralin + dimethylbenzofuran, 11: ethyltetralin, 12: ethyletralin, 13: biphenyl + hexahydroacenaphthene, 14: phenylether, 15: C_4-indene, 16: C_4-tetralin, 17: C_3-dihydronaphthalene, 18: tetradecahydroanthracene, 19: tetradecahydrophenanthrene, 20: C_3-dihydronaphthalene, 21: C_4-tetralin, 22: C_5-indan or C_4-tetralin, 23: C_5-indan or C_4-tetralin, 24: C_4-dihydronaphthalene, 25: hexadecahydropyrene, 26: octahydroanthracene.

TABLE 4. Alteration in Chemical Composition of SRC-II Distillate Due to Hydrotreatment for Five Compound Classes(d,e)(4)

Material	Phenols(a)		N-heterocycles(b)		Primary Aromatic Amines(b)		Aromatics and Hydroaromatics(a)		Polynuclear Aromatics(c)	
Feedstock	Σphenols	130	ΣN-heterocycles	28	Σprimary aromatic amines	1.9	Σaromatics + hydroaromatics	450	Σpolynuclear aromatics	110
	C_1 phenols	41	quinoline	3.6	aminonaphthalenes	0.09	naphthalene	97	$C_{14}H_{10}$	38
	C_2 phenols	35	C_1 quinoline	1.4	aminoanthracene/ aminophenanthrene	0.07	C_1 naphthalenes	82	$C_{16}H_{10}$	9.2
	phenol	27	carbazole	1.3	aminobiphenyls	0.03	C_2 naphthalenes	65	$C_{18}H_{12}$	3.5
	C_3 phenols	16	C_2 quinoline	0.8	aminopyrene/ aminofluoranthene	0.03	tetralin	57	benzo(a)pyrene	0.041
	o-cresol	9	acridine	0.1	aminochrysene	0.02	C_1 tetralin	26	benzo(e)pyrene	0.077
					aminocarbazoles	trace	biphenyl	24		
Moderately Hydrotreated	Σphenols	30	ΣN-heterocycles	1.2	Σprimary aromatic amines	≤0.005	Σaromatics + hydroaromatics	660	Σpolynuclear aromatics	18
	C_1 phenols	5.5	tetrahydroquinoline	0.08	none detected	≤0.005	tetralin	71	$C_{14}H_{10}$	2.5
	C_2 phenols	2.6	tetrahydrocarbazole	0.06			C_2 tetralins	51	$C_{16}H_{10}$	0.8
	phenol	1.6	carbazole	0.04			C_1 tetralins	48	$C_{18}H_{12}$	0.4
	C_3 phenols	1.2	C_1 quinoline	0.03			C_1 naphthalenes	41	benzo(a)pyrene	≤0.010
			tetrahydroazapyrene	0.02					benzo(e)pyrene	≤0.010
Severely Hydrotreated	Σphenols	17	ΣN-heterocycles	1.0	Σprimary aromatic amines	≤0.005	Σaromatics + hydroaromatics	780	Σpolynuclear aromatics	7.5
	C_1 phenols	4.3	tetrahydrocarbazole	0.07	1 none detected	≤0.005	C_1 tetralins	120	$C_{14}H_{10}$	1.9
	C_2 phenols	2.1	tetrahydroquinoline	0.05			C_2 tetralins	41	$C_{16}H_{10}$	0.5
	phenol	1.2	carbazole	trace			tetralin	34	benzo(a)pyrene	≤0.010
	C_3 phenol	0.8	C_1 quinoline	trace			C_3 tetralins	27	benzo(e)pyrene	≤0.005

(a) Estimated directly in the unfractionated material by GC and GCMS.
(b) Estimated in the basic fraction by GCMS. Concentrations given have been calculated for the unfractionated material.
(c) Estimated in the unfractionated material and in the PAH fraction by GC and GCMS. Concentrations given have been calculated for the unfractionated material.
(d) The contributions listed do not total 100% due to the presence of compound classes not listed (e.g., aliphatics) and losses during extraction. Specific compounds listed under each heading are those found in the highest concentrations within that class.
(e) Concentrations are given in parts per thousand.

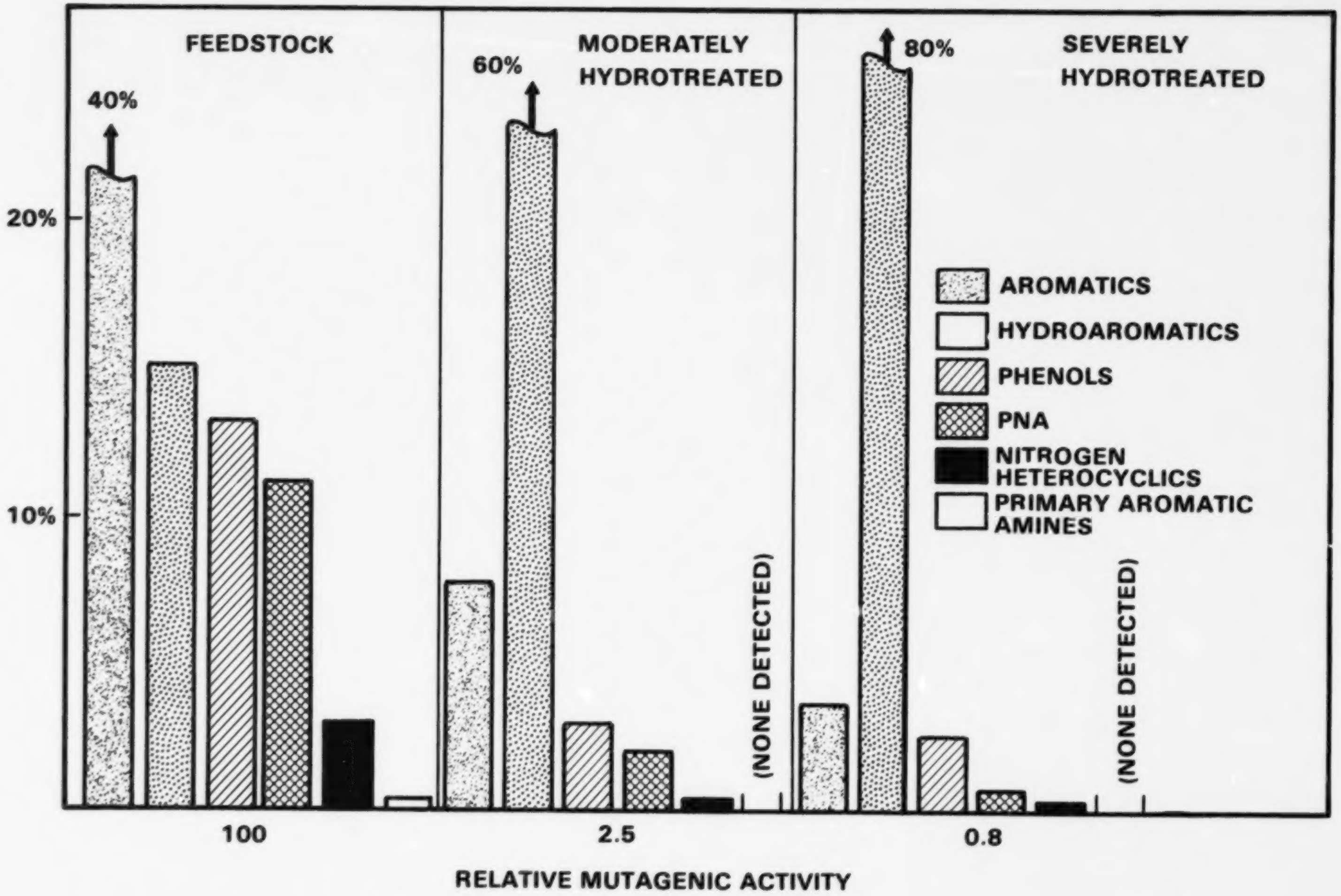

FIGURE 8. Gross Chemical Composition Related to Severity of Hydrotreatment(4)

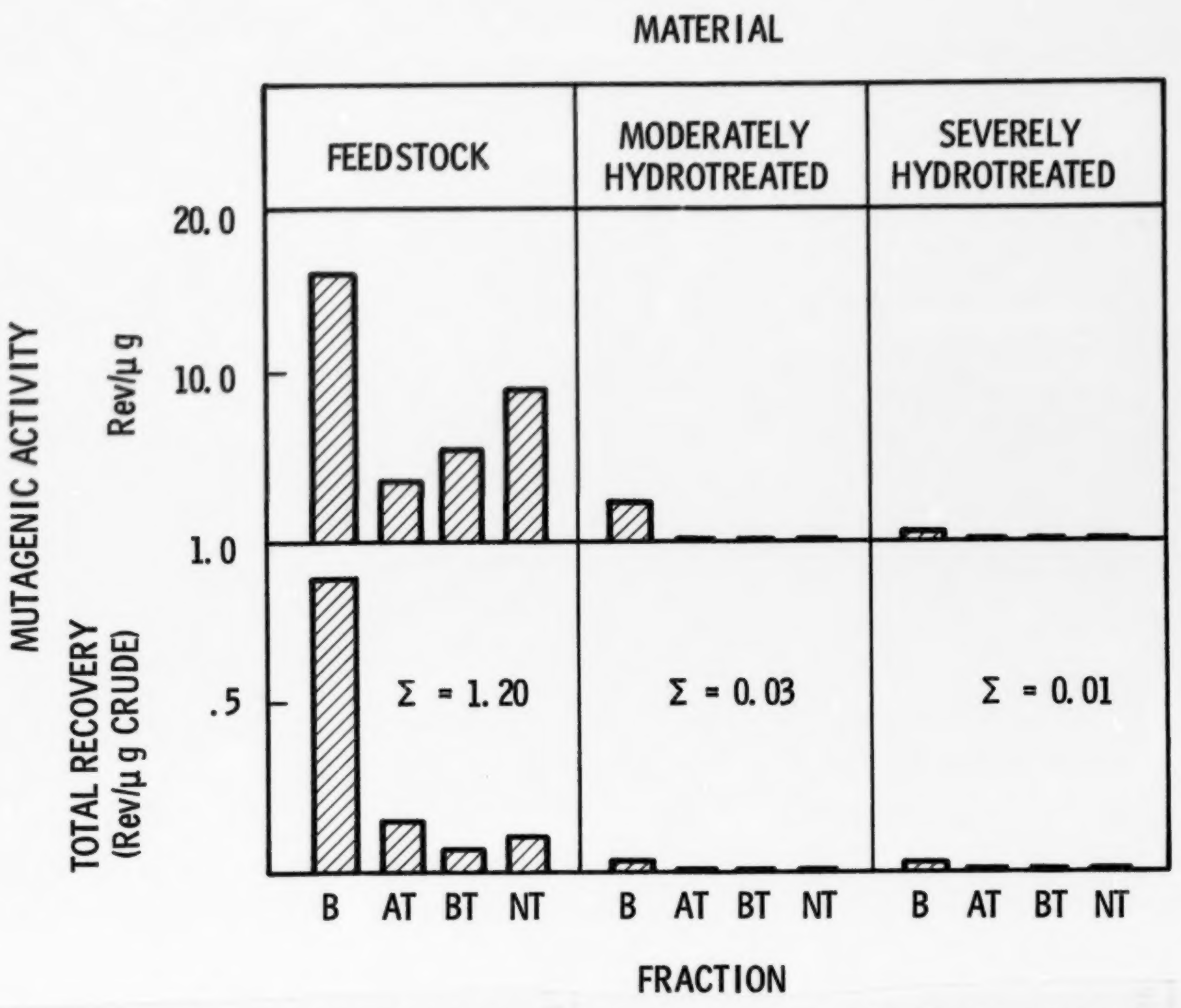

FIGURE 9. Specific and Weighted Activity Test Results for the Basic (B), Base Induced tar (AT) acid induced tar (BT) and isooctane induced tar (NT) from Raw and Hydrotreated SRC-II Distillate Blend. (a) Strain TA98 with S9 enzyme activation. (b) Specific activity weighted by the gravimetric yield of the fraction.(4)

TABLE 5. The Effect of Catalytic Hydrogenation on the Mutagenicity of SRC-II Coal Liquid(4)

Material	Chemical Fraction[b]	Percent of Total Wt.	Revertants per μg Fraction[c]	Weighted Response, rev/μg[a]	Total Weighted Response, rev/μg	Total Revertants Unfractionated Material, rev/μg
Feedstock	Basic	5.37	16.2	0.86	$\sum = 1.20$	2.54
	Acid Induced Tar	5.97	2.7	0.16		
	Base Induced Tar	1.40	5.6	0.08		
	Isooctane Insoluble Tar	1.16	8.9	0.10		
Moderately Hydrotreated	Basic	1.44	2.2	0.03	$\sum = 0.03$	None detected above backbround
	Acid Induced Tar	0.06	0	0		
	Base Induced Tar	0.03	0	0		
	Isooctane Insoluble Tar	0.44	0	0		
Severely Hydrotreated	Basic	0.99	0.79	0.01	$\sum = 0.01$	None detected above background
	Acid Induced Tar	1.31	0	0		
	Base Induced Tar	0.03	0	0		
	Isooctane Insoluble Tar	0.44	0	0		

(a) (Revertants per μg) x (percent total weight)/100.
(b) Other fractions were not active.
(c) Strain TA98 with S9 enzyme activation.

those compound classes in coal liquids which are primarily responsible for induction of mutagenic activity, namely, the nitrogen containing aromatics and especially the primary aromatic amines as well as reduction of the concentrations of polynuclear aromatic hydrocarbons. Other biological assays including mammalian cell culture and skin painting studies are also under way but are not reported in detail here. Generally, there has been relatively good agreement among the assays used. Table 6, a comparison of data from three biological assays, demonstrates this agreement. Differences do show up, however, in the results from 2-aminoanthracene and for heavy distillate. The mutagenic activity of 2-aminoanthracene is very high whereas tumorigenic activity is only moderate. The reverse is true for heavy distillate; tumorigenicity is high whereas mutagenicity is moderate relative to standard control compounds.(3)

Information such as reported here will obviously have some impact upon the development of a liquefaction industry. Samples used were selected with engineering guidance. Criteria included suitability and relevance to future demonstration or commercial design and operation. However, since one can, in practice, only anticipate or scale up to a limited number of the conditions in a final design configuration, caution must be applied in the application of pilot plant derived data. Certainly further data is required. But more important, interaction between chemists, biologists, ecologists and process engineers must be on a continuous basis such that pertinent and meaningful data is prepared within a time frame commensurate with the process development.

TABLE 6. Comparison of Mutagenic and Carcinogenic Activity for Several Crude Fossil-Derived Materials

Material	Ames Assay	Mammalian Cell Culture	Skin Tumorigenesis
Light distillate	---	---	---
Heavy distillate	++	++	++++
Shale oil	+	+	++
Crude petroleum	--	slight	+
Benzo(a)pyrene	++	++	+++
2-Aminoanthracene	++++	+++	++

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LOW-NO_x COMBUSTORS FOR ALTERNATE FUELS CONTAINING SIGNIFICANT QUANTITIES OF FUEL-BOUND NITROGEN

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ABSTRACT

This paper summarizes data generated on two EPA-sponsored programs concerned with the development of low-NO_x combustors for high nitrogen containing fuels. EPA Contract 68-02-3125 is concerned with NO_x production and control from liquid fuels containing significant quantities of bound nitrogen. It was found that fuel nitrogen content is the primary composition variable affecting fuel NO formation and that emissions from both petroleum and alternative liquid fuels correlate with total fuel nitrogen content. Conditions were identified which allow high-nitrogen fuels to be burned satisfactorily with minimal NO_x emissions. Certain coal-derived fuel gases may contain ammonia. Data is presented from a series of bench-scale reactors designed to minimize the conversion of this ammonia to NO_x. Lowest NO_x emissions were produced in a rich/lean combustor utilizing either a diffusion flame or a catalyst in the fuel-rich primary stage.

SECTION 1

INTRODUCTION

Combustion of liquid fuels derived from petroleum sources accounts for a significant fraction of fossil fuel consumption in stationary combustors. As petroleum reserves grow smaller, the United States is projected to place heavy reliance on coal, the most abundant fossil fuel available, in the search for new energy supplies. Coal can be burned directly or converted into either a liquid or a gaseous fuel. The potential for low sulfur emissions makes combustion of gasified coal an environmentally attractive alternative to direct-fired coal combustion. However, low-Btu coal gases can contain ammonia concentrations as high as 0.38 percent (1). In a conventional combustor, much of this ammonia may be converted to nitrogen oxides resulting in significant pollutant emission: up to 1370 ng/J (3.2 lbm/10^6 Btu) for full conversion of NH_3 to NO_2.

A balanced fuel economy necessitates that in the future many industrial users will burn petroleum and coal- or shale-derived liquid fuels. Since these liquid fuels have relatively high nitrogen content and low hydrogen-to-carbon ratios, there will be the potential for adverse environmental impact due to the increased emission of combustion-generated pollutants unless preventative measures are taken (1-2). The pollutant of major concern in this paper is nitrogen oxides (NO_x). The paper addresses the impact of switching from conventional fuels to alternative gaseous or liquid fuels and of the mechanisms of combustion modification techniques used to control NO_x emissions.

Alternative liquid fuels can be broadly classified as those synthesized from the products of coal gasification, and those derived directly as liquids. The fuels in the first category tend to be clean, low-boiling-point fuels such as alcohols, and are essentially free from nitrogen and sulfur; thus, their impact upon pollutant emissions is minimal. The liquids in the second category may be compared to crude petroleum oils containing a wide range of hydrocarbon compounds with boiling points from 300°K to greater than 900°K. The bound nitrogen content of crude synfuels is generally higher than petroleum crudes, and for many applications it might be necessary to upgrade the fuel by removing the nitrogen. Recognizing that alternative liquid fuels contain more bound nitrogen than the petroleum fuels that they would be replacing, one key factor in their production is to what extent combustion modification will allow control of NO_x emissions and reduce the necessity for substantial denitrification, thereby reducing the cost of synfuels.

Nitrogen oxides produced during combustion emanate from two sources. Thermal NO is formed by the fixation of molecular nitrogen and its formation rate is strongly dependent upon temperature (3). Fuel NO is formed by the oxidation of chemically-bound nitrogen in the fuel by reactions with a weak temperature dependence, but a strong dependence upon oxygen availability (4-5-6-7). Thus, those emission control techniques which minimize peak flame temperature by the addition of inert diluents (e.g., cooled recycled combustion products or water addition) minimize thermal NO formation, but have a minor impact upon fuel NO production. Staged heat release (staged combustion) provides the most effective NO_x control technique for nitrogen-containing fuels because fuel NO formation is mainly dependent upon local stoichiometry. It can be accomplished either by separating the combustion chamber into two zones and dividing the total combustion air into two streams, or by appropriate burner design which promotes localized fuel-rich conditions.

Minimizing fuel NO_x formation requires the existence of a fuel-rich primary combustion zone to maximize the conversion of fuel nitrogen to molecular nitrogen since the fate of fuel-bound nitrogen is strongly controlled by the reactant stoichiometry. Many studies (8-12) have shown that under fuel-rich conditions the efficiency of conversion to N_2 increases significantly. Thus, there are two fuel nitrogen reaction paths leading to the production of N_2 or NO, namely:

Path A. Fuel-lean

$$XN + \text{Oxidant} \rightarrow NO + \ldots.$$

Path B. Fuel-rich

$$XN + \ldots. \rightarrow N_2 + \ldots.$$

The objective of staged combustion emission control techniques is the provision of conditions which maximize N_2 production via Path B. Two factors of practical importance are the residence time and the stoichiometry required to maximize N_2 production in the fuel-rich primary zone.

If the residence time is insufficient, then the original fuel nitrogen species will exist in the gaseous state as some XN compound which can be converted to NO in the second-stage heat release zone. The stoichiometry required to achieve minimum XN concentrations at the exit of the primary stage will be determined by (1) the rate of evolution of nitrogen species from the fuel; (2) the inevitable distribution of stoichiometries from fuel-rich to fuel-lean which occurs because the primary zone is supplied by a diffusion flame; and (3) the overall temperature of the primary zone. From equilibrium considerations the total fixed nitrogen (TFN given by $NO + HCN + NH_3$) is a minimum at approximately 65 percent theoretical air with levels less than 10 ppm depending upon temperature and fuel C/H ratio. Exhaust NO_x emissions are considerably greater than levels predicted by equilibrium, suggesting the existence of kinetic limitations in the fuel-rich primary stage.

NO_x formation during combustion of alternate fuels is not well-understood; however, recent test results have indicated that replacing a petroleum oil with a coal- or shale-derived liquid may result in a major increase in NO_x emissions. Bench-scale experiments (13) have shown that the smoke and combustion characteristics of the SRC-II coal liquids are equivalent to light oil, but uncontrolled NO_x emissions are high due to the 0.8 to 1.2 percent N in the fuel. Pilot-scale SRC-II studies (14-16) have demonstrated that both fuel blending and staged combustion are effective in reducing NO_x emissions and that improved atomization, increased preheat, and increased excess O_2 increase NO_x. Full-scale testing (17) has confirmed the need for optimized combustion modifications. Similar results have also been achieved during bench-scale (18) and field tests (19) with shale-derived liquids.

SECTION 2

EXPERIMENTAL SYSTEMS

The experimental systems used to investigate NO_x formation from gaseous and liquid fuels have been described in detail elsewhere and only a brief summary will be presented in this paper.

LBG GAS STUDIES

The apparatus for the bench-scale experiments can be divided into four subsystems: LBG supply, modular combustors, sample train and control systems. A simplified schematic of the facility can be seen in Figure 1.

Synthetic LBG was produced from hot air premixed with vaporized water and heptane passed through a catalytic reformer. The reformer was operated at pressures between 6.4 and 11.9 atmospheres at a stoichiometry of 45 percent theoretical air, the richest stoichiometry attainable without excessive sooting. The water acts as a diluent to maintain the maximum catalyst bed temperature at around $1370^{o}K$. The reformer product gas passed through a variable heat exchanger, cooling it to the desired preheat temperature. Ammonia and methane are added to trim the gas to the desired fuel nitrogen and hydrocarbon content. The LBG passed through a soot filter and into a valve system, controlling the fraction of the LBG which goes to the combustors and the fraction which is bypassed. If none of the gas was bypassed, maximum combustor capacity was 60,000 J/s (200,000 Btu/hr).

The combustors consisted of a series of modules with 5 cm (2 in) ID reaction/flow chambers enclosed in 15 cm (6 in) OD low-density insulation and housed in flanged steel pipe. Primary ignition modules include the catalyst and the diffusion flame. Secondary burnout was achieved in the jet-stirred secondary air injector. Plug flow modules of various lengths allowed control of primary and secondary residence times. The primary ignition modules are shown in Figure 2. In the catalyst module, premixed LBG and primary air passed through a stainless steel flow straightener/flame arrestor and into the graded cell catalyst. The catalyst, supplied by Acurex, consisted of three zirconia honeycomb monoliths of decreasing cell size, coated with nickel oxide. Platinum had been added to the coating of the upstream monolith to promote ignition. In the concentric diffusion flame module, LBG is introduced

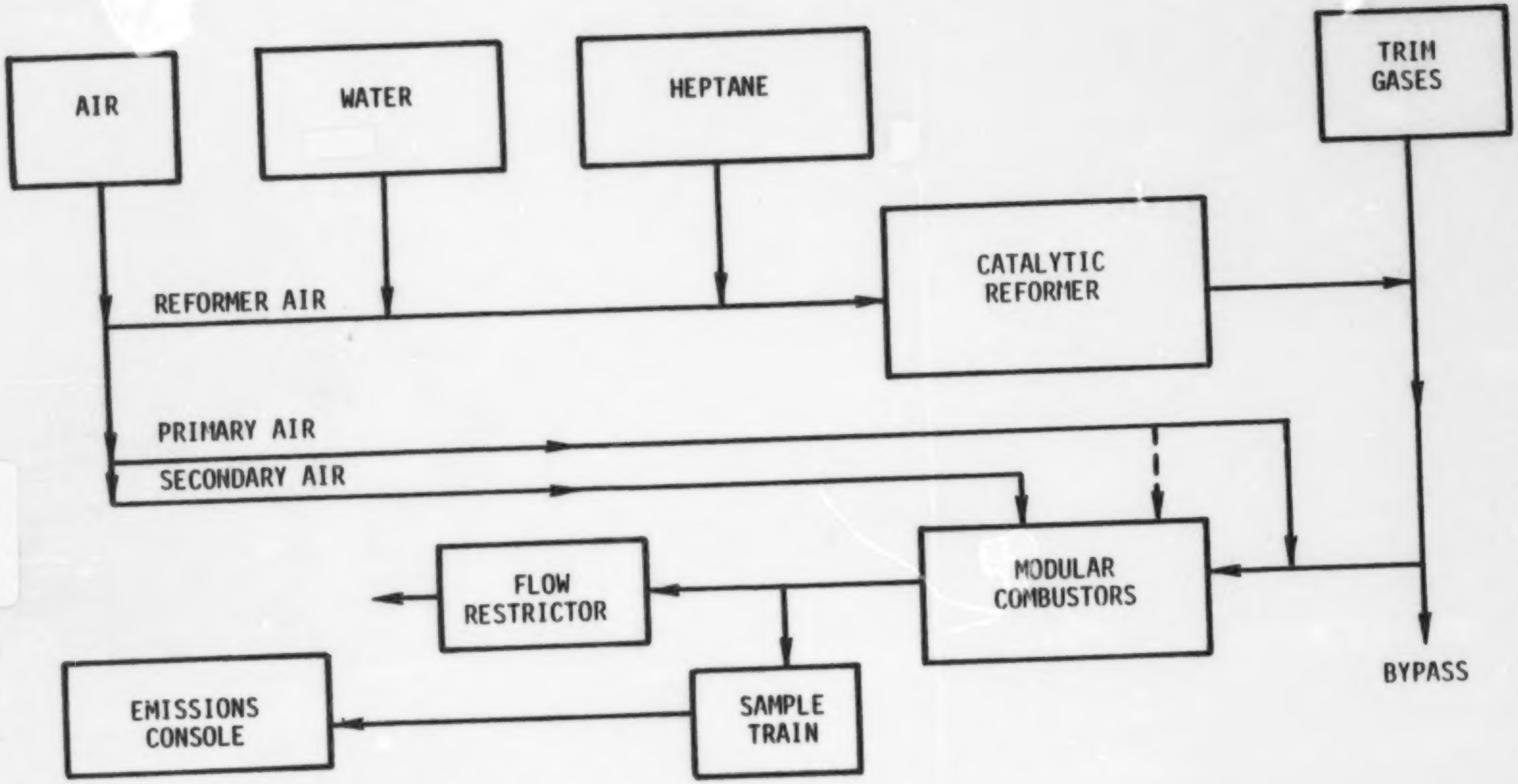
AIR
WATER
HEPTANE
TRIM GASES
REFORMER AIR
CATALYTIC REFORMER
PRIMARY AIR
SECONDARY AIR
MODULAR COMBUSTORS
FLOW RESTRICTOR
BYPASS
EMISSIONS CONSOLE
SAMPLE TRAIN

Figure 1. Bench-Scale Pressurized Test Facility.

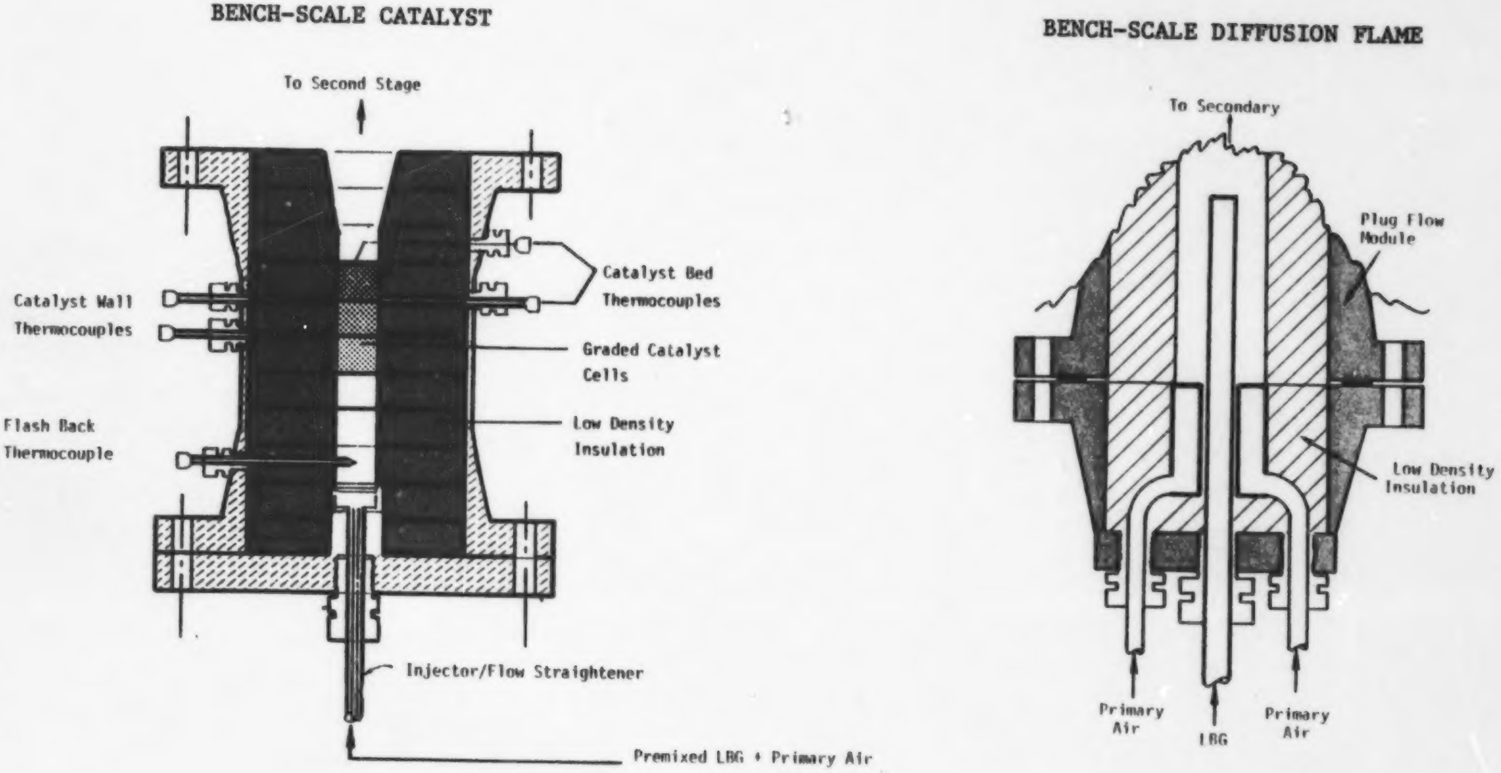
BENCH-SCALE CATALYST
To Second Stage
Catalyst Wall Thermocouples
Flash Back Thermocouple
Catalyst Bed Thermocouples
Graded Catalyst Cells
Low Density Insulation
Injector/Flow Straightener
Premixed LBG + Primary Air
BENCH-SCALE DIFFUSION FLAME
To Secondary
Plug Flow Module
Low Density Insulation
Primary Air
LBG
Primary Air

Figure 2. Primary Ignition Modules.

through a removable fuel tube of variable diameter. Straightened primary air passes annularly around the fuel tube in the direction of the fuel flow.

Samples are taken in the secondary region, through a water-cooled stainless steel probe situated on the centerline of the flow chamber. The cooling water is preheated and the stainless steel sample lines are wrapped with heat tape to maintain the sample system above the dewpoint of the exhaust gases. The sample stream is throttled to nearly atmospheric pressure.

LIQUID-FIRED TUNNEL FURNACE

The downfired tunnel furnace illustrated in Figure 3 was designed to allow utilization of commercially-available spray nozzles, and yet be capable of testing with artificial atmospheres. This combustor, which has been described in detail elsewhere (6), was 2.1 m long and 20 cm in inside diameter. The walls consisted of insulating and high-temperature castable refractories and the full-load firing rate was 0.53 cc/sec, which corresponds to a nominal heat release of 20 kW. All airstreams were metered with precision rotameters. The main combustion air was preheated with an electric circulation heater; the atomization air was not preheated. In certain tests the "air" was enriched or replaced with varying amounts of carbon dioxide, argon, and oxygen, all of which were supplied from high-pressure cylinders.

ANALYTICAL SYSTEMS

Exhaust concentrations were monitored continuously using a chemiluminescent analyzer for NO and NO_x, a NDIR analyzer for CO and CO_2, and a paramagnetic analyzer for O_2. The flue gas was withdrawn from the stack through a water-cooled, stainless steel probe using a stainless steel/Teflon sampling pump. Sample conditioning prior to the instrumentation consisted of an ice bath water condenser and glass wool and Teflon fiber filters. All sample lines were 6.3 mm Teflon and all fittings 316 stainless steel.

In-flame temperature measurements were made with a standard suction pyrometer containing a platinum/rhodium thermocouple. In-flame gas samples were withdrawn with a long, stainless steel water-quench probe. HCN and NH_3 were absorbed in a series of wet impingers and concentrations determined using specific ion electrodes. Sulfide ion interference was minimized by the addition of lead carbonate (20). Hydrocarbons were measured using a water-cooled probe, heated sample line, and an FID analyzer.

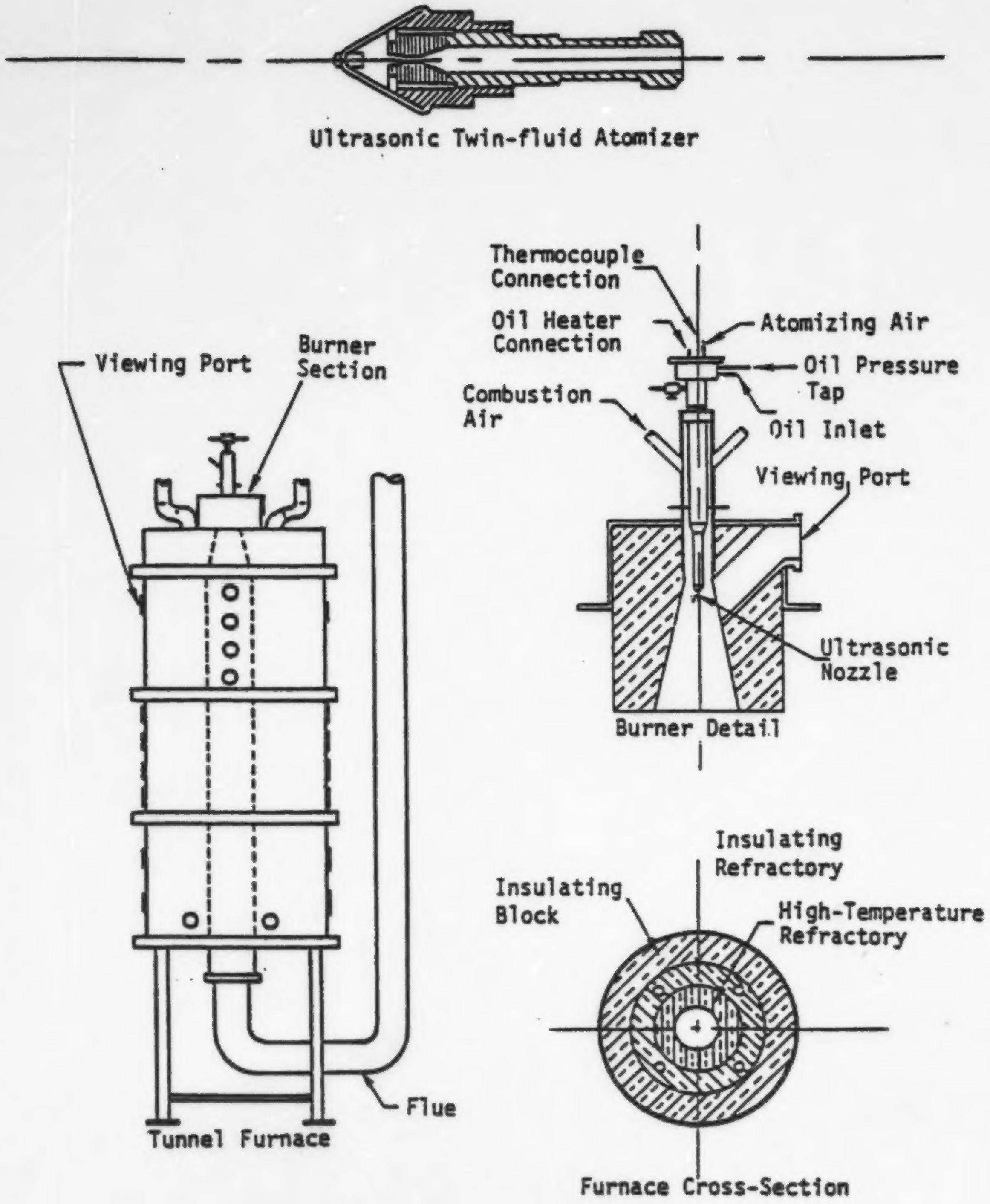
Ultrasonic Twin-fluid Atomizer
Viewing Port
Burner Section
Flue
Tunnel Furnace
Thermocouple Connection
Oil Heater Connection
Atomizing Air
Oil Pressure Tap
Combustion Air
Oil Inlet
Viewing Port
Ultrasonic Nozzle
Burner Detail
Insulating Refractory
Insulating Block
High-Temperature Refractory
Furnace Cross-Section

Figure 3. Details of the Tunnel Furnace System.

LIQUID FUELS

Figure 4 illustrates the wide spectrum of composition for the distillate oils (half-filled symbols), heavy petroleum liquids (open symbols), and alternative liquid fuels (solid symbols) investigated to date. The petroleum-derived fuels had sulfur contents ranging from 0.2 to 2.22 percent with a maximum nitrogen content of 0.86. The nitrogen content of the alternative fuels range from 0.24 to 2.5 percent. Table 1 lists the complete chemical analysis and physical properties of each fuel as determined by an independent laboratory. The shale liquids included crude shale from the Paraho process (A3) and four refined products: diesel fuel marine (DFM, A1) residual fuel oil (A5), a 520-to-850°F distillation cut (A7), and a 5.75/1 medium/heavy SRC-II blend (A6), a heavy SRC-II distillate (A9), and an SRC-II blended with the donor solvent (A4).

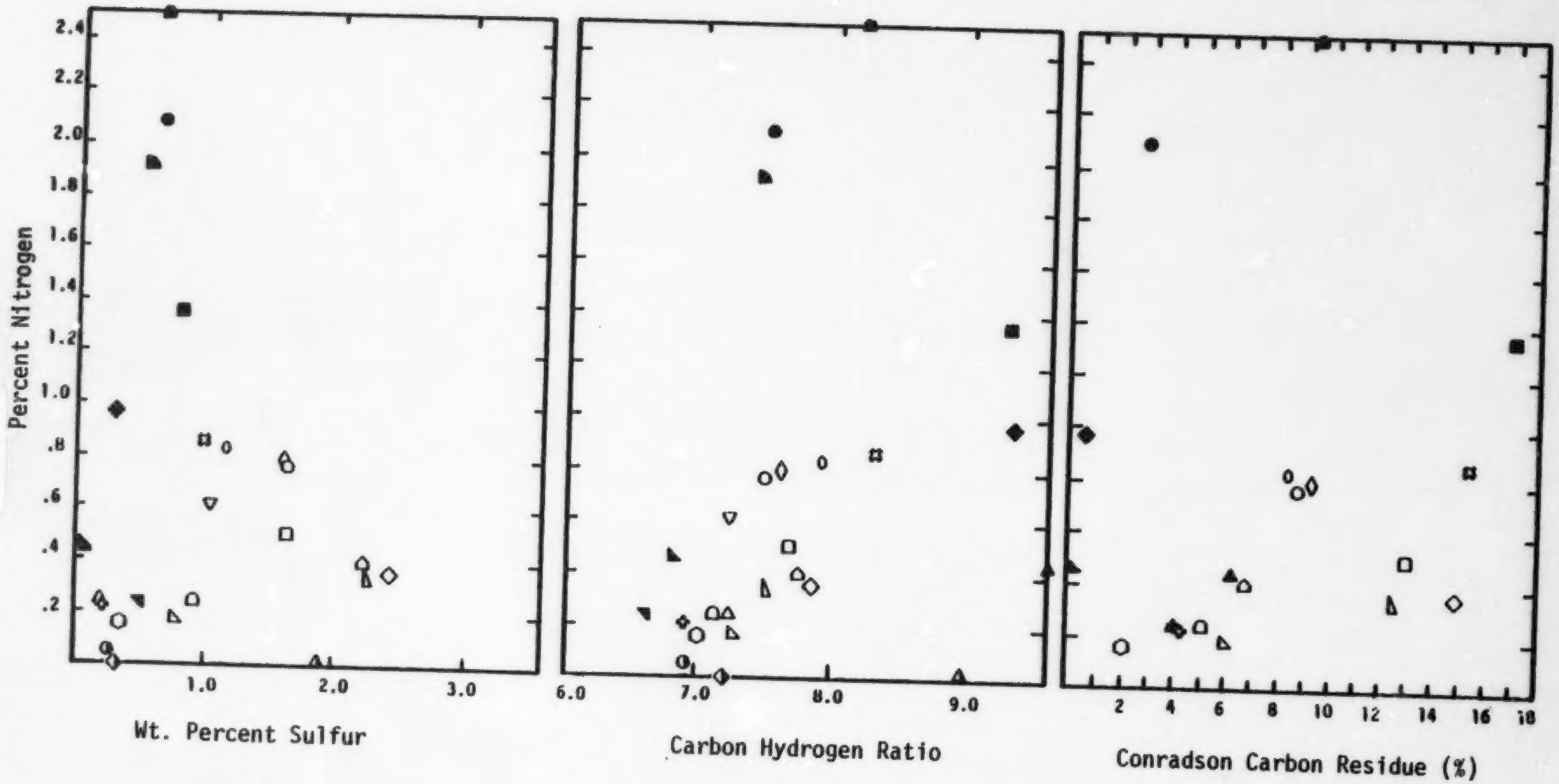

Figure 4. Properties of Fuels Tested.

Table 1. Detailed Fuel Analyses

	D1	D2	D3	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
	Alaskan Diesel	W. Texas Diesel	California No. 2 Oil	East Coast	Middle East	Low Sulfur No. 6 Oil	Indo/ Malaysian	Venezuelan Desulphurized	Pennsylvania (Amarada Hess)	Gulf Coast	Venezuelan	Alaskan	California
Symbol	◆	▲	◐	⬡	◺	✙	△	∩	⊿	◇	⌂	□	▽
Ultimate Analysis:													
Carbon, %	86.99	88.09	86.8	86.54	86.78	86.57	86.53	85.92	84.82	84.62	85.24	86.04	85.75
Hydrogen, %	12.07	9.76	12.52	12.31	11.95	12.52	11.93	12.05	11.21	10.77	10.96	11.18	11.83
Nitrogen, %	0.02	0.026	0.053	0.16	0.18	0.22	0.24	0.24	0.34	0.36	0.40	0.51	0.62
Sulfur, %	0.31	1.88	0.27	0.36	0.67	0.21	0.22	0.93	2.26	2.44	2.22	1.63	1.05
Ash, %	<.001	<.001	<.001	0.023	0.012	0.02	0.036	0.033	0.067	0.027	0.081	0.034	0.038
Oxygen, %	0.62	0.24	0.36	0.61	0.41	0.46	1.04	0.83	1.3	1.78	1.10	0.61	0.71
				2.1	6.0	4.4	3.98	5.1	12.4	14.8	6.8	12.9	
Conradson Carbon Residue, %				0.34	3.24	0.94	0.74	2.59	4.04	7.02	8.4	5.6	
Asphaltene, %				205	350	325	210	176	275	155	210	215	
Flash Point, °F				50	48	105	61	48	66	40	58	38	
Pour Point, °F				24.9	19.8	25.1	21.8	23.3	15.4	13.2	14.1	15.6	19.5
API Gravity at 60°F	33.1	18.3	32.6	131.2	490	222.4	199	113.2	1049	835	742	1,071	246.1
Viscosity, SSU, at 140°F	33.0	32.0	30.8	45	131.8	69.6	65	50.5	240	181	196.7	194	70.00
at 210°F	29.5	28.8	29.5										
Heat of Combustion:													
Gross Btu/lb			19,330	19.260	19,070	19,110	19,070	18,400	18,520	18,240	18,240	18,470	
Net Btu/lb				18,140	17,980	17.970	17,980	17,300	17,500	17,260	17,400	17,580	
Calcium, ppm				7.1	1.2	9.52	14	8.7	9.2	4.4	9.1	6.9	
Iron, ppm				16	2.6	123.6	16	6.5	13.2	19	11	24	
Maganese, ppm				0.09	0.02	0.46	0.13	0.09	0.10	0.13	0.09	0.06	
Magnesium, ppm				3.7	0.08	2.23	3.6	3.6	3.3	0.4	3.8	1.4	
Nickel, ppm				6.7	13	14.10	19		32.7	29	52	50	
Sodium, ppm				37	0.98	3.74	15		64.5	3.6	32	37	
Vanadium, ppm				14	25	3.11	101		81.5	45	226	67	

Table 1. Detailed Fuel Analyses (Continued)

	R11	R12	R13	R14	A1	A2	A3	A4	A5	A6	A7	A8	A9
	California	California	California	California (Kern County)	Shale-Derived DFM	Synthoil	Crude Shale	SRC II Blend	Shale Residual	SRC II	Shale Fraction (520-850°F)	Shale Fraction (+850°F)	SRC II Heavy Distillate
	○	◇	¤	0	◥	■	●	▲	◣	◆	◗	▮	⬟
Ultimate Analysis:													
Carbon, %	85.4	85.33	86.66	86.61	86.18	86.30	84.6	89.91	86.71	85.91	85.39	85.92	88.98
Hydrogen, %	11.44	11.23	10.44	10.93	13.00	7.44	11.3	9.27	12.76	8.74	11.53	10.61	7.64
Nitrogen, %	0.77	0.79	0.86	0.83	0.24	1.36	2.08	0.45	0.46	(0.96)	1.92	2.49	1.03
Sulfur, %	1.63	1.60	0.99	1.16	0.51	0.80	0.63	0.065	0.28	0.30	0.72	0.63	0.39
Ash, %	0.043	0.032	0.20	0.030	0.003	1.56	.026	0.004	0.009	0.04	0.002	0.24	0.058
Oxygen, %	0.71	1.02	0.85	0.44	1.07	2.54	1.36	0.30	0.03	4.08	0.44	0.11	1.90
Conradson Carbon Residue, %	8.72	9.22	15.2	8.3	4.1	23.9	2.9	6.18	0.19	0.51	0.07	9.3	
Asphaltene, %	5.18	5.18	8.62	3.92	0.036	16.55	1.33	4.10	0.083		0.12	4.24	
Flash Point, °F		150	180	255	182	210	250	70	235	1.73	255	370	265
Pour Point, °F	38	30	42	65	40	80	80	<-72	90	-55	70	95	8
API Gravity at 60°F	15.4	15.1	12.6	12.3	33.1	S=1.14	20.3	10.0	29.0	( )	22.3	12.0	1.3
Viscosity, SSU, at 140°F	854	748.0	720	4630	36.1	10,880	97	40.6	54.3	39	62.9	3050	67.2
at 210°F	129	131.6	200	352	30.7	575	44.1	32.5	37.3	( )	41.8	490	41.3
Heat of Combustion:													
Gross Btu/lb	18,470	18,460	18,230	18,430	19,430	16,480	18,290	17,980	19,350	17,100	18,520	18,000	17,120
Net Btu/lb	17,430	17,440	17,280	17,430	18,240	15,800	17,260	17,130	18,190		17,470	17,030	16,240
Calcium, ppm	21	14	90.6	4.4	0.13	1,670	1.5	0.33	4.20		<.05	238	
Iron, ppm	73	53	77.2	15	6.3	109	47.9	3.9	<0.5		2.9	86	
Manganese, ppm	0.8	0.1	0.87	0.15	0.06	6.2	0.17	<0.5	<0.5		0.033	1.3	
Magnesium, ppm	5.1	3.8	31.4	1.1		170	5.40	0.17	0.15		0.021	51	
Nickel, ppm	65	82	88.0	68	0.43	2.6	5.00	<0.5	<0.5		<0.5	7.4	
Sodium, ppm	21	2.6	22.3	3.4	0.09	148	11.71	0.31	2.51		<0.1	11	
Vanadium, ppm	44	53	66.2	39	<.1	6.5	<.3	<1.0	<1.0		<0.2	1.1	

SECTION 3

RESULTS - LBG GAS

Encouragingly low NO_x levels have been achieved on the bench scale utilizing a catalytic reactor and a diffusion flame reactor. An effective fuel nitrogen-reducing catalyst was identified in laboratory-scale experiments and the effects of scale and stoichiometry were examined in the bench-scale experiments. A fuel-lean diffusion flame was identified as an attractive low-NO_x combustor concept in laboratory-scale experiments and effects of scale, stoichiometry, hydrocarbon content of the fuel, fuel tube size, pressure, and primary residence time were examined in the bench-scale experiments.

Effects of catalyst type on fuel nitrogen processing in LBG combustion were examined on the laboratory scale in an unstaged catalytic reactor operated at a constant adiabatic flame temperature of 1473°K. Figure 5 shows the variable stoichiometry results for two catalysts. The alumina supported platinum catalyst converted almost all fuel nitrogen to NO_x in fuel-lean combustion and had a minimum conversion of 40 percent in fuel-rich combustion. At stoichiometries richer than 60 percent theoretical air, decreasing NO concentrations were overwhelmed by increasing NH_3, and HCN concentrations, causing a sharp rise in ΣXN. The zirconia supported platinum/nickel oxide catalyst converted 80 percent of the fuel nitrogen to NO_x in lean combustion, but had very low conversions in rich combustion. For a 500 ppm NH_3 in LBG dopant level, less than 10 ppm ΣXN were measured at stoichiometries as rich as 40 percent theoretical air. Tests of the platinum/nickel oxide catalyst over a range of adiabatic flame temperatures (1273-1673°K) and with CH_4 as the fuel yielded similar results.

A rich/lean series staged platinum/nickel oxide primary catalytic reactor was selected as a potential low NO_x concept for bench scale testing. The scale-up results were in general agreement with the laboratory-scale results. Figure 6 compares the results of staged combustion of a 500 ppm NH_3 doped LBG at two scales: 1200 and 20,000 J/sec (4000 and 70,000 Btu/hr). Each had high conversions of NH_3 to NO_x in fuel-lean combustion. Minimum conversions occurred

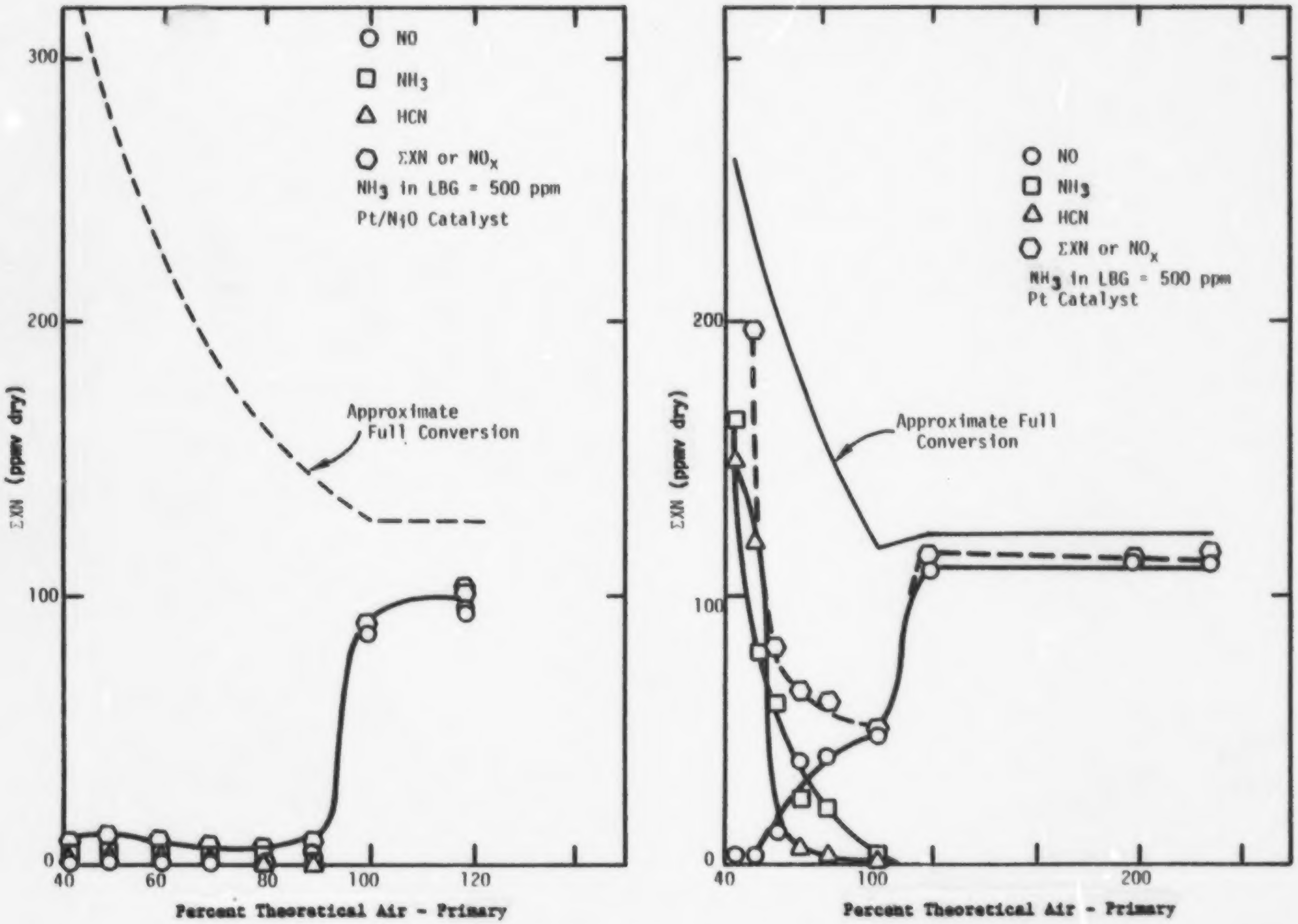

Figure 5. Laboratory Scale Catalyst Comparison.

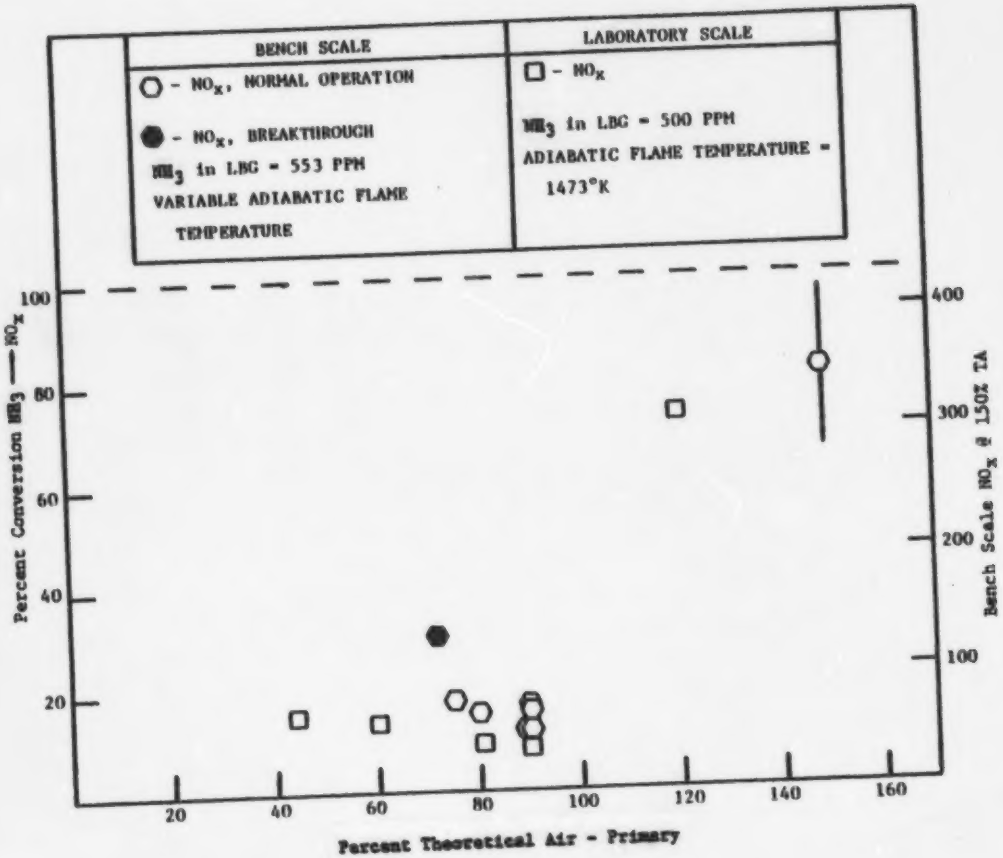

Figure 6. Pt/NiO Catalyst Scale-up.

in rich/lean staged combustion when the primary was operated close to stoichiometric. At a primary stoichiometry of 90 percent theoretical air, the laboratory-scale catalytic reactor converted 8 percent of the input NH_3 to NO_x while the bench-scale combustor had an overage conversion of 14 percent. Conversions in the bench-scale combustor remained low (less than 18 percent) over all rich primary stoichiometries under normal operation; but breakthrough occurred if the primary was operated richer than 75 percent theoretical air: the temperatures on the walls of the catalyst monoliths dropped and the conversion rose sharply. Breakthrough was not observed in the laboratory-scale experiment where the adiabatic flame temperature was maintained at a constant $1473^{\circ}K$ by varying the amount of nitrogen diluent in the reactants. The undiluted flame reactor LBG had a higher heating value (HHV) of 6.7×10^6 J/m^3 (180 Btu/ft^3) while the HHV of the bench-scale LBG was only 3.0×10^6 J/m^3 (80 Btu/ft^3). This indicates that raising the heating value of the gas could extend the operating range of the Pt/NiO catalyst, and that catalyst effectiveness is limited by a threshold flame temperature below which breakthrough occurs.

It is difficult to compare the laboratory and the bench-scale diffusion flame combustors. Figure 7 shows laboratory- and bench-scale results for diffusion flame combustion of LBG containing about 500 ppm NH_3 and varying amounts of methane. In the unstaged laboratory-scale experiment, performed at atmospheric pressure in a cold-wall reactor under attached laminar-flow conditions, the hydrocarbon content of the LBG had the most significant effect on XN conversion. Conversions as low as 10 percent were observed for combustion of hydrocarbon-free LBG under nearly stoichiometric conditions. Under richer conditions, conversion increased due primarily to increasing ammonia concentrations. However, under leaner conditions conversions remained quite low. Similar trends were observed in combustion of LBG containing 5 percent methane, but XN conversion was much higher. In the staged bench-scale experiment, performed at 8 atmospheres in a nearly adiabatic combustor under turbulent-flow conditions, effects of hydrocarbon content and stoichiometry were not so pronounced.

The bench-scale flame was not visible and there was no reliable indicator as to whether the flame was attached or lifted. However, throughput and tube size ranged from conditions where the flame should definitely be

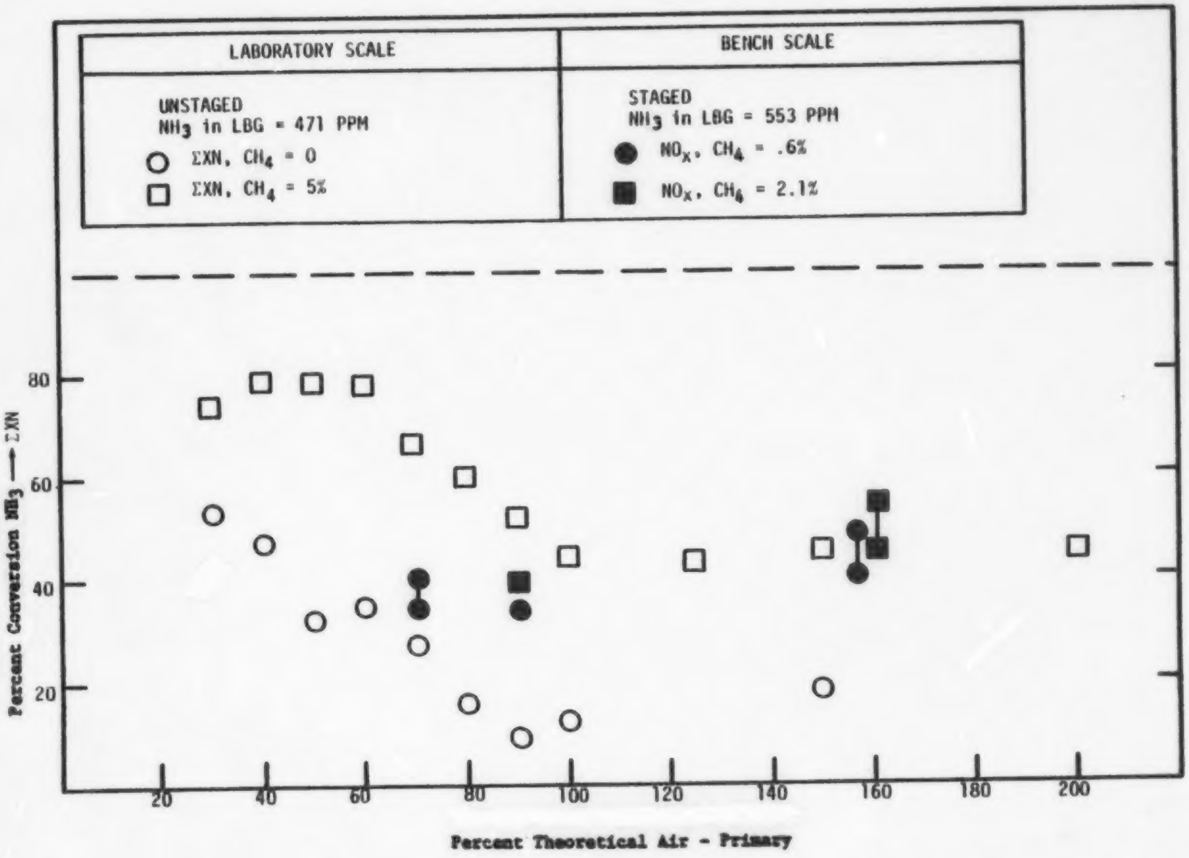

Figure 7. Diffusion Flame Scale-up.

attached to conditions where the flame should definitely be lifted. No sharp changes were observed in NO_x emissions or in other measured parameters, indicating that the attached/lifted transition was not an important factor. This agreed with previous variable-throughput laboratory-scale tests of a hydrocarbon-containing diffusion flame, where a smooth NO_x transition was observed as the flame became detached (3).

Figure 8 shows the effect of fuel tube size on XN conversion in the bench-scale diffusion flame operated at 8 atmospheres. In constant-pressure operation at a fixed stoichiometry, fuel flow and primary residence time were independent of fuel tube size, while Reynolds number was inversely proportional to the fuel tube I.D., fuel tube size had little effect on XN conversion in fuel-rich combustion. However, in lean combustion, increasing tube size (decreasing Reynolds number) decreased NH_3 conversion to NO_x. Increased tube size also decreased the NO_x noise level (high frequency concentration fluctuation shown by the error bars in the figure), perhaps an indication of flame stability.

Figure 9 shows the effect of pressure on rich/lean and lean diffusion flames. In the bench-scale system, pressure is maintained by passing the exhaust gases through a critical-flow orifice. For a fixed stoichiometry, fuel flow and Reynolds number are proportional to pressure while primary residence time is independent of pressure. The staged tests were performed at a primary stoichiometry of about 95 percent theoretical air. For low-hydrocarbon LBG, NH_3 conversion to NO_x remained constant at 33 percent over pressures ranging from 4 to 8 atmospheres. For LBG containing 2.1 percent CH_4, conversions remained constant around 40 percent with changing pressure. The lean tests were performed at a stoichiometry of about 150 percent theoretical air. Noise levels were higher than in the staged case. Conversions increased slightly with increasing pressure in low hydrocarbon combustion. Little change in conversion was seen with changing pressure for the 2.1 percent CH_4 LBG.

Primary residence time appeared to have the most pronounced affect on XN conversion in a staged diffusion flame. Residence time was varied at constant pressure by changing the pressure control orifice size. In constant-pressure operation at a fixed stoichiometry, fuel flow and Reynolds number were inversely proportional to primary residence time. Figure 10 shows XN

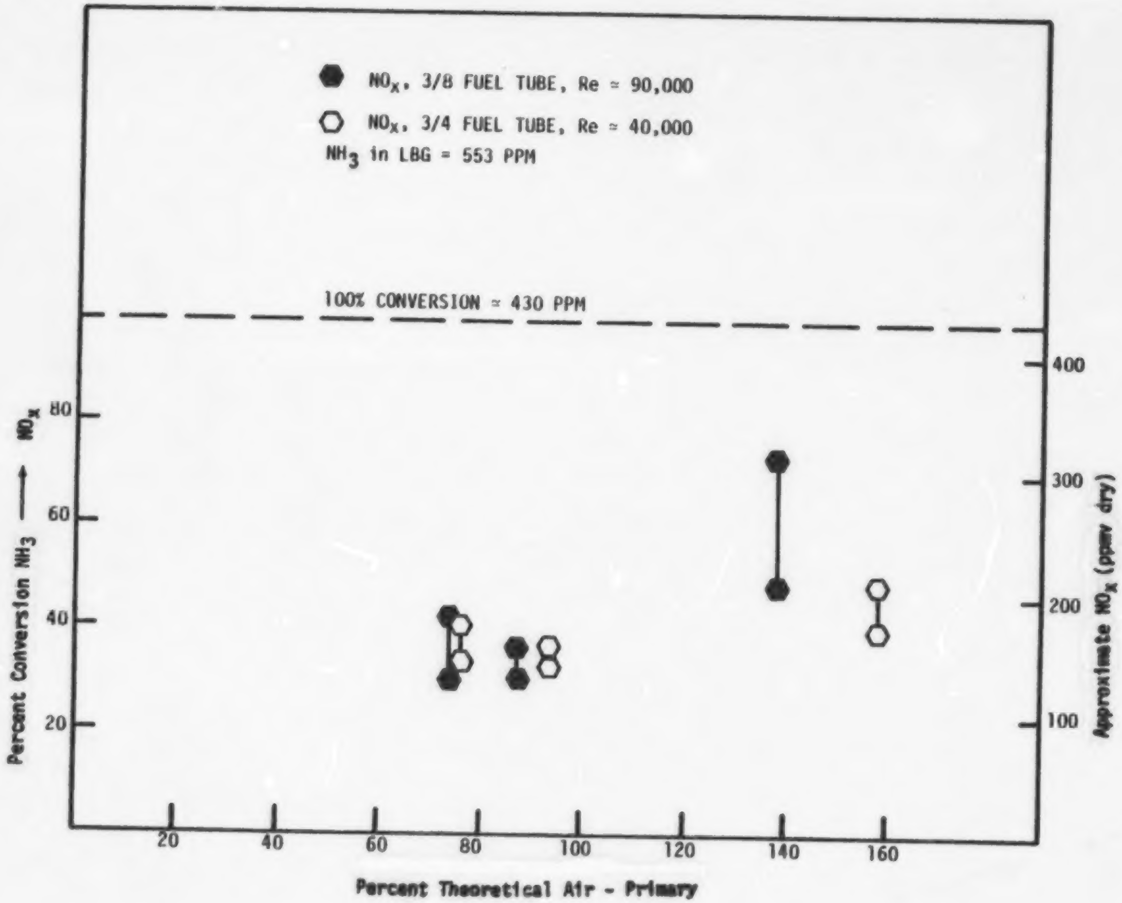

Figure 8. Bench-Scale Diffusion Flame: Effect of Reynolds Number.

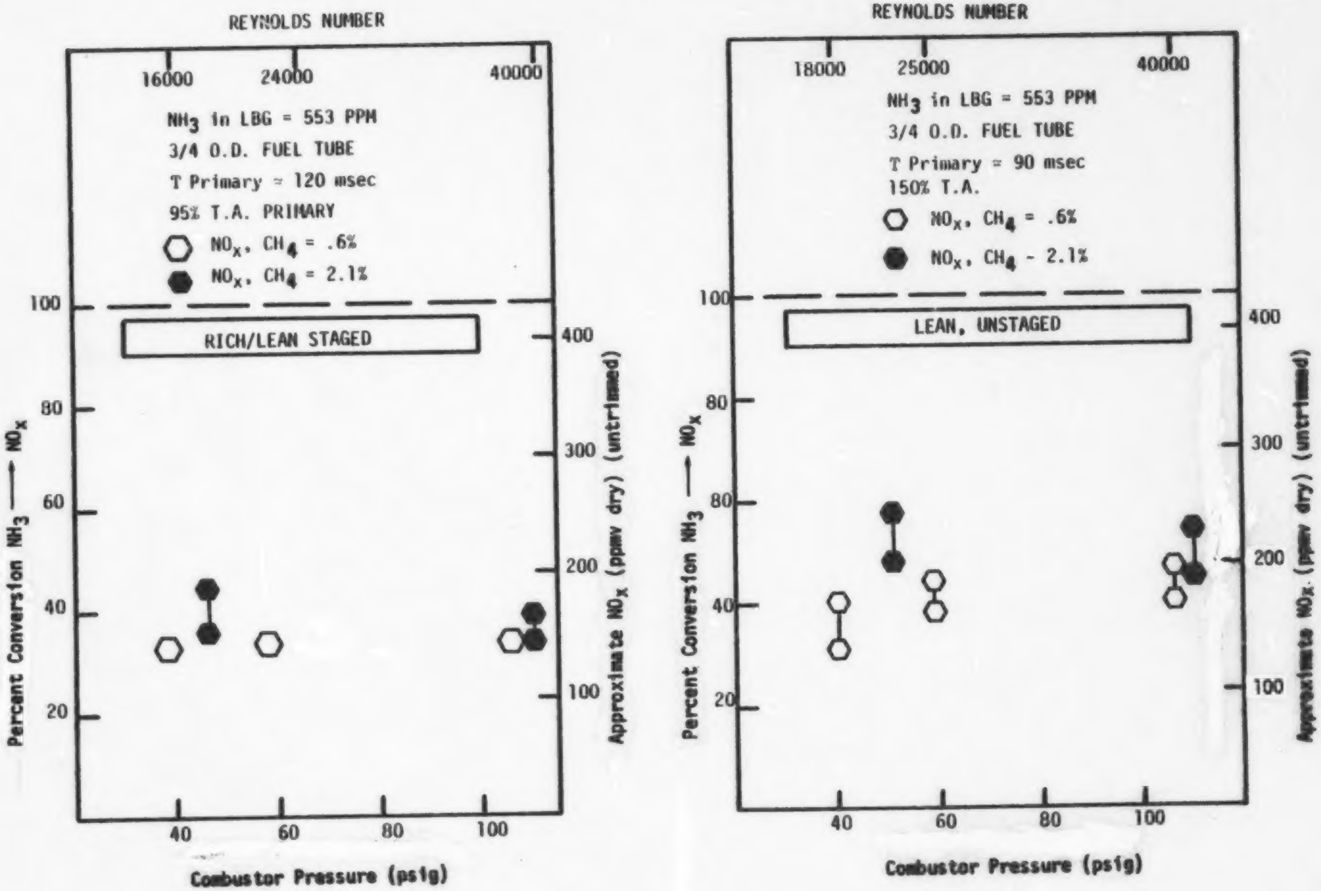

Figure 9. Bench-Scale Diffusion Flame: Variable Pressure/Reynolds Number.

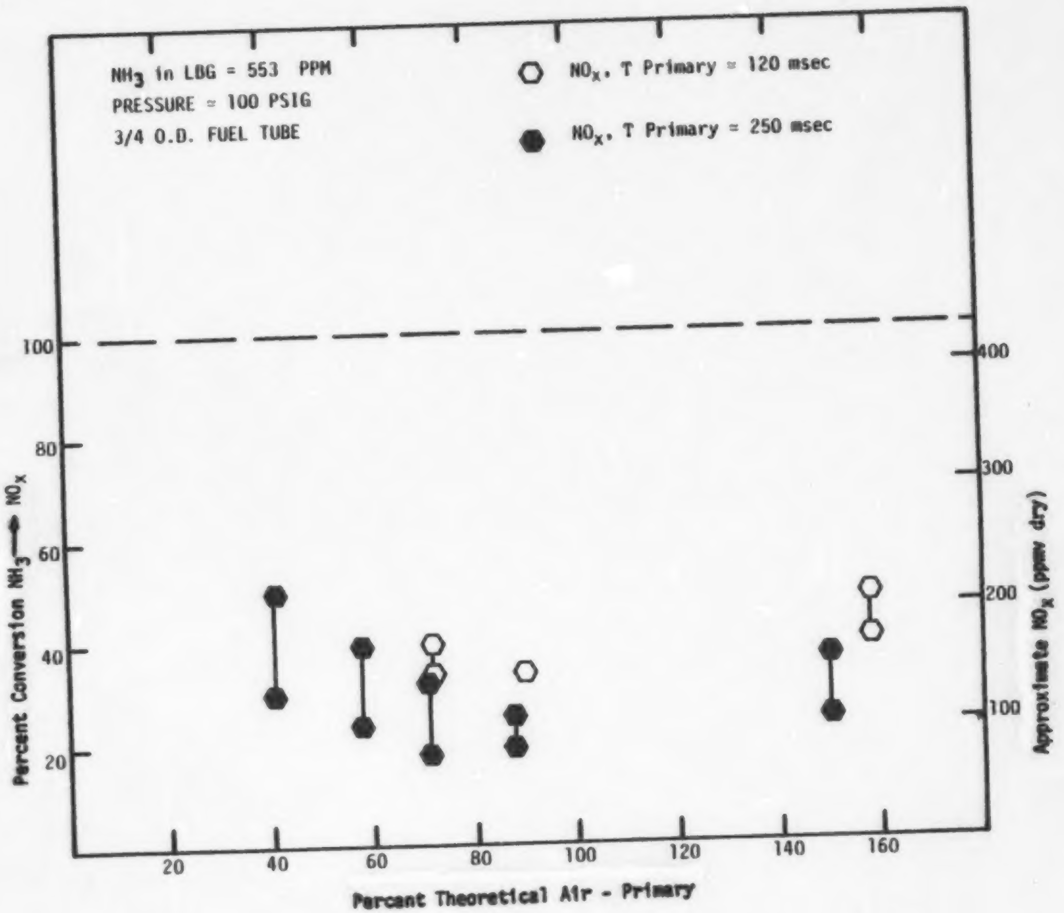

Figure 10. Bench-Scale Diffusion Flame: Effect of Residence Time.

conversion with primary stoichiometry for two different primary residence times. Using a large pressure-control orifice, a pressure of 8 atmospheres was achieved at fuel-tube Reynolds numbers around 40,000 and primary residence times around 120 msec. A minimum XN conversion of 34 percent was observed at a primary stoichiometry around 90 percent theoretical air. Using a smaller pressure control orifice, a pressure of 8 atmospheres was achieved at fuel-tube Reynolds numbers around 20,000 and primary residence times around 250 msec. A minimum XN conversion of about 22 percent was observed at a primary stoichiometry around 90 percent theoretical air. For a 553-ppm-doped LBG burned out to 150 percent theoretical air, this XN minimum corresponded to a NO_x concentration of 100 ppm.

Figure 11 shows NO_x concentration as a function of NH_3 in the LBG for rich/lean staged combustion in a diffusion flame and in a platinum/nickel oxide catalytic combustor. For both the catalytic and the diffusion-flame combustors, NO_x emissions increased with increasing fuel nitrogen content, but the increase in NO_x was much less than proportional to the increase in fuel nitrogen content. The 3/8 OD tube diffusion flame, operated at a primary stoichiometry of 76 percent theoretical air and a pressure of 4.4 atmospheres, converted 40 percent of its fuel nitrogen to NO_x at 553-ppm NH_3 in the LBG and had conversions of only 11 percent at a 3800-ppm doping level. The catalyst, operated at a primary stoichiometry of 80 percent theoretical air and a pressure of 2.4 atmospheres, had XN conversions of 16 percent at the low NH_3 doping level and 6 percent at the high doping level. Similar trends, but higher NO_x concentrations, were observed for both combustors in fuel-lean combustion.

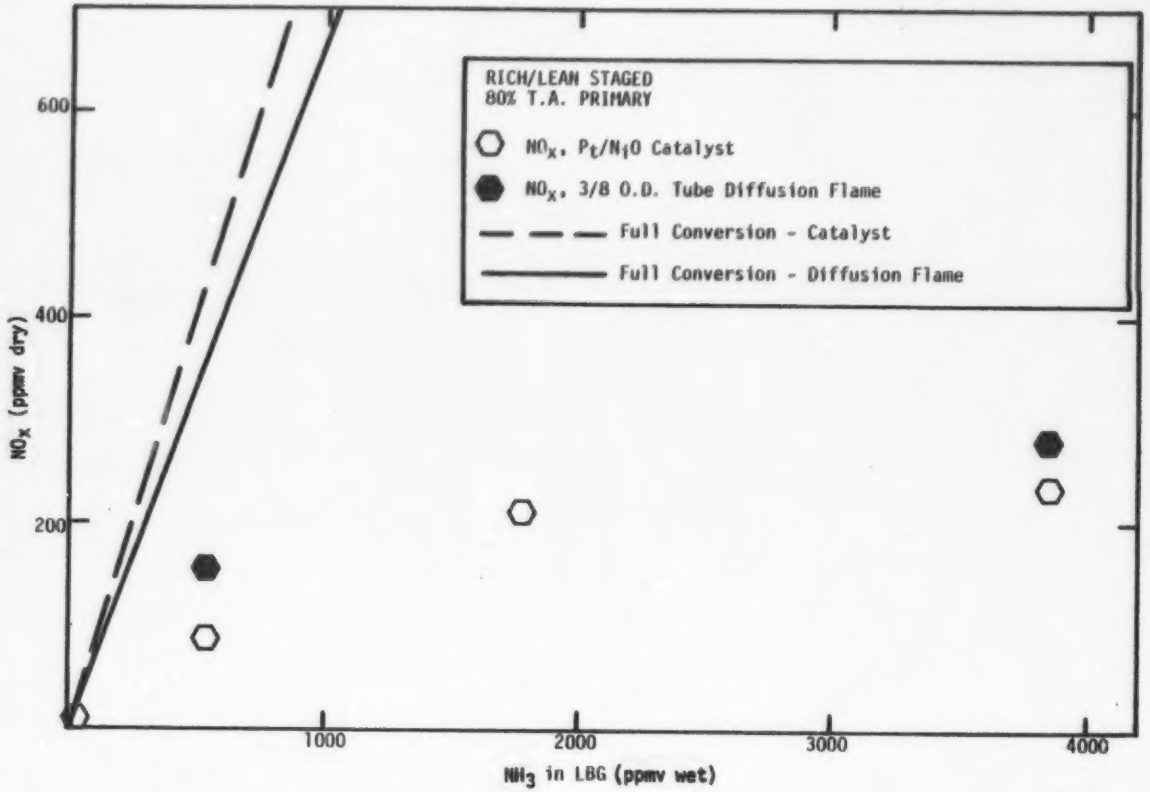

Figure 11. Bench-Scale Reactor Comparison: Effect of Dopant Level.

SECTION 4

LIQUID FUEL - EXCESS AIR RESULTS

PETROLEUM LIQUIDS

To define the influence of fuel composition on total and fuel NO_x emissions, each oil was tested under similar conditions in the tunnel furnace. Fuel NO_x formation was determined by substitution of the combustion air with a mixture of argon, oxygen, and carbon dioxide. The argon replaced the nitrogen, thereby eliminating thermal NO_x formation and the CO_2 provided the proper heat capacity so that flame temperatures were matched. Total and fuel NO_x emissions were measured with an air preheat level of 405 $\pm 5^{\circ}$K and an atomization pressure of 15 psig. Figure 12 presents a composite plot for total and fuel NO_x (defined by argon substitution) as a function of weight percent nitrogen in the fuel for a wide range of petroleum and blended distillate fuels. In Figure 12 the various symbols represent different base fuels (see Table 1 for symbol key). Those symbols shown with a line refer to distillate or residual fuels doped with pyridine or thiophene. It can be seen that both total and fuel NO_x increase with increasing fuel nitrogen content, and that total fuel nitrogen level is the dominant factor controlling fuel NO_x formation in this system. The form of the nitrogen does not appear to significantly influence fuel NO formation under excess air conditions, as doping with a volatile nitrogen compound (pyridine) resulted in NO_x emission similar to that from a less volatile residual oil of the same nitrogen content. Since the data is for a system where very fine oil droplets (approximately 25 micron mean diameter) are well-dispersed in the oxidizer under hot fuel-lean conditions, it is not surprising that fuel NO_x emissions are somewhat higher than those achieved in practical systems.

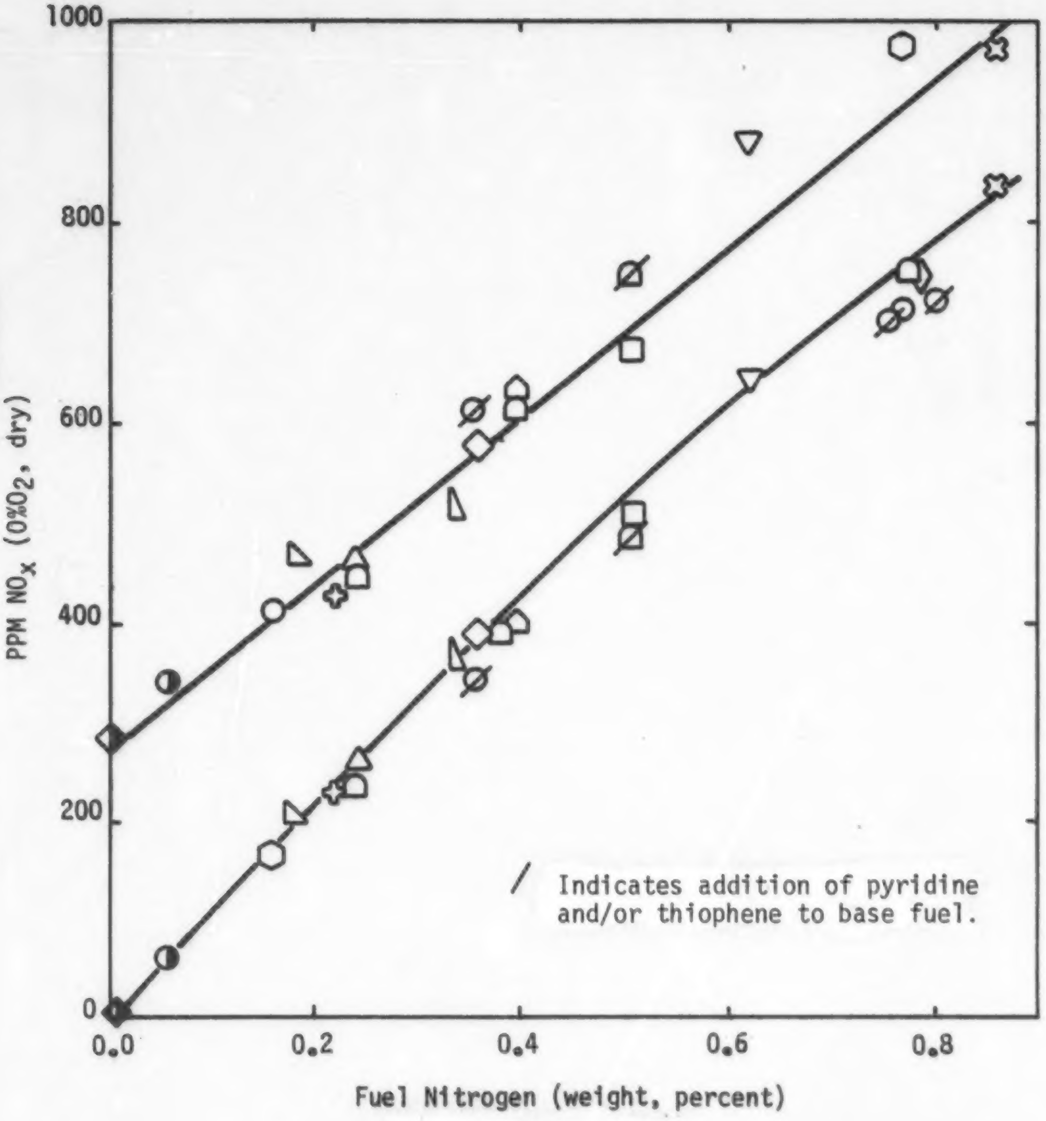

Figure 12. Total and Fuel NO_x Emissions From Pure and Doped (pyridine and thiophene) Petroleum Fuels Tunnel Furnace.

ALTERNATIVE FUELS

Figure 13 presents a composite plot of total and fuel NO_x for the range of petroleum fuels together with alternative fuels and mixtures. The Paraho shale was mixed with the same low sulfur oil used by Mansour (19). Synthoil could not be pumped without blending and the results presented in Figure 4 refer to 80 and 90 percent Synthoil blends with distillate oil. The SRC-II blend refers to a mixture of SRC-II and the donor solvent. Under the conditions tested, fuel NO_x emissions increase approximately linearly with increasing fuel nitrogen and it can be seen that the fate of fuel nitrogen in alternative fuels is similar to that in petroleum-derived fuels. Figure 14 presents the fuel NO_x data plotted as a percentage of the fuel nitrogen converted to fuel NO_x. For low fuel nitrogen contents, the conversion decreases rapidly (from greater than 90 percent) as fuel N increases. Eventually, however, the conversion becomes almost independent of fuel nitrogen content; hence, the linear dependence shown in Figure 13.

The absolute level of the fuel N conversion can be influenced by altering the fuel/air contacting and/or the fuel atomization (2), but the results obtained in this study suggest that fuel nitrogen is the only first-order fuel composition parameter controlling NO_x formation in fuel-lean flames. This conclusion applies to petroleum-, coal-, and shale-derived liquid fuels. However, there appear to be second-order effects where the volatility of the fuel nitrogen compound does have an influence upon fuel NO_x formation. Comparison of the data for the fuels with fuel nitrogen content of approximately 0.24 percent indicates that the highest conversion is achieved with a shale-derived distillate fuel with a large volatile nitrogen fraction.

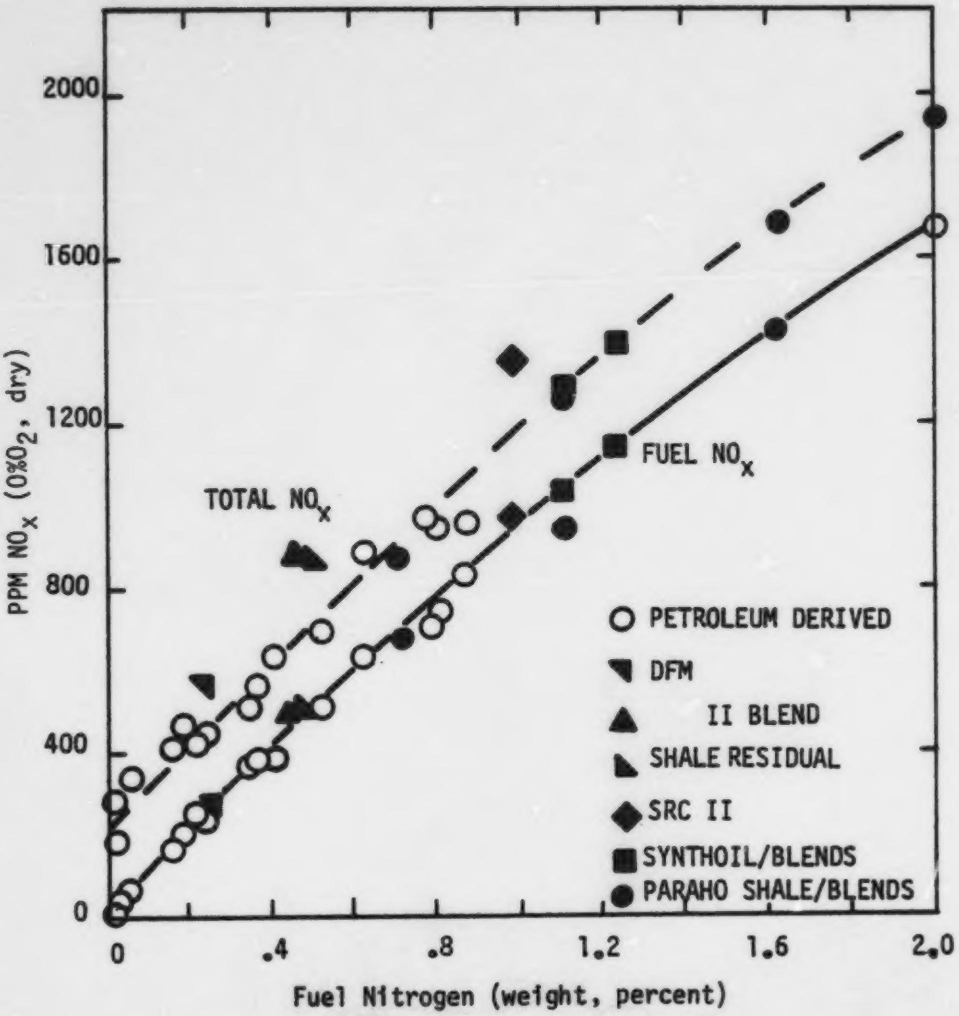

Figure 13. The Effect of Fuel Nitrogen Content on Total and Fuel NO$_x$ (5 percent excess oxygen).

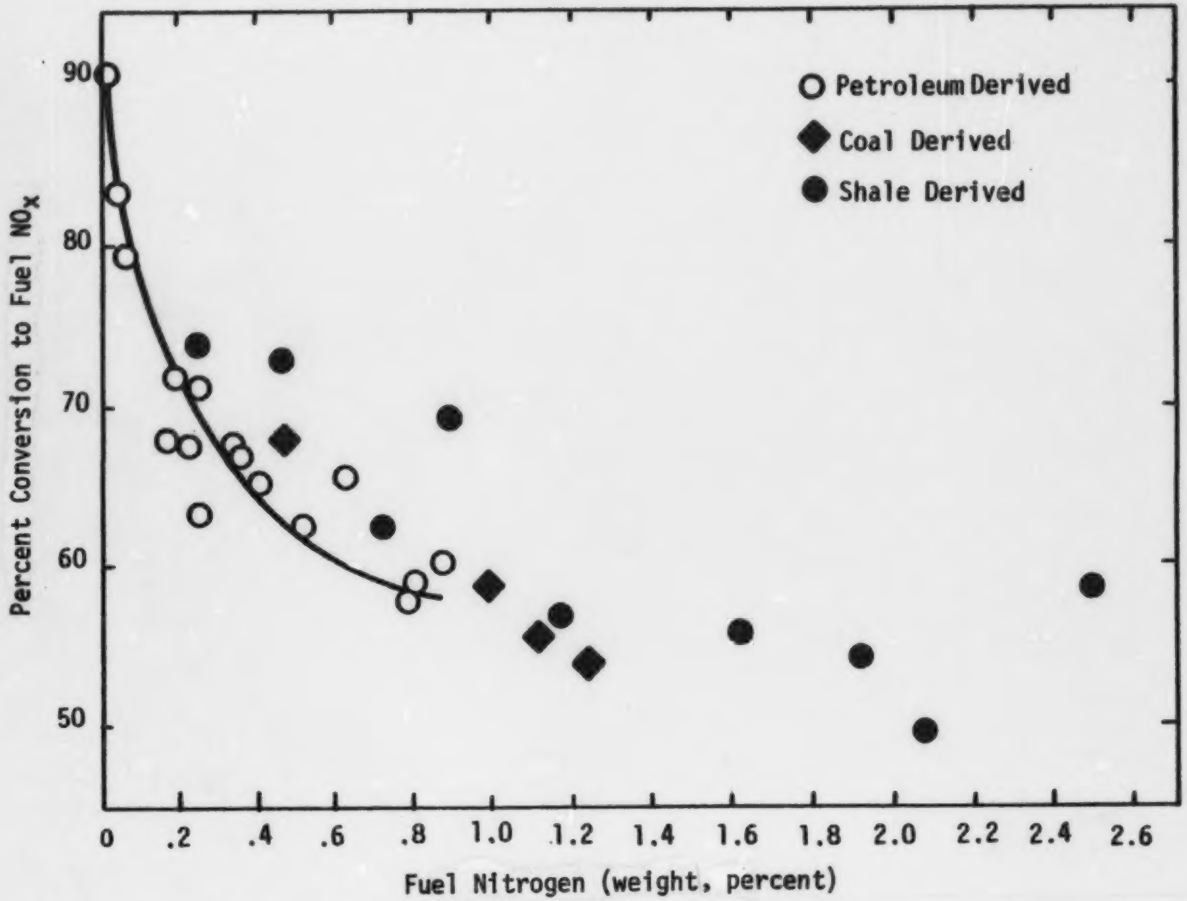

Figure 14. Fuel Nitrogen Conversion - Comparison of Alternate and Petroleum-Derived Fuels.

SECTION 5

LIQUID FUELS STAGED COMBUSTION RESULTS

POTENTIAL FOR NO_X CONTROL

Staged combustion, i.e., the operation of a combustion system in which the fuel originally burns under oxygen-deficient conditions, provides the most cost-effective control techniques established to date for reducing fuel NO_x. Figure 15 shows the influence of primary zone stoichiometric ratio on total NO_x emissions for two coal-derived and two shale-derived liquids under staged combustion conditions and 3 percent overall excess O_2. All the data in Figure 15 were obtained in the tunnel furnace with ultrasonic atomization and with a first-stage residence time of approximately 800 ms. As the primary zone becomes more fuel-rich, NO_x emissions decrease dramatically to a minimum and then increase again. This trend is in agreement with previously-reported data on petroleum fuels (21).

FUEL CHEMISTRY

First Stage Stoichiometry

In an effort to better understand the mechanisms of NO formation under staged combustion conditions, the original furnace was modified to allow in-flame sampling of the XN (NO, HCN, NH_3) species and cooling of the first-stage and/or second-stage combustion products, as illustrated in Figure 16. A "radiation shield" (choke) was installed near the top of the furnace to minimize the effects of downstream changes on the fuel vaporization zone. A secondary air injection ring and cast refractory choke were installed at 41 in. to insure isolation of the first stage. Variable cooling was achieved by insertion of multiple stainless steel water-cooling coils.

Figures 17, 18, and 19 show typical results of the detailed in-flame measurements made at the exit of the first stage for a distillate oil (D1-Alaskan

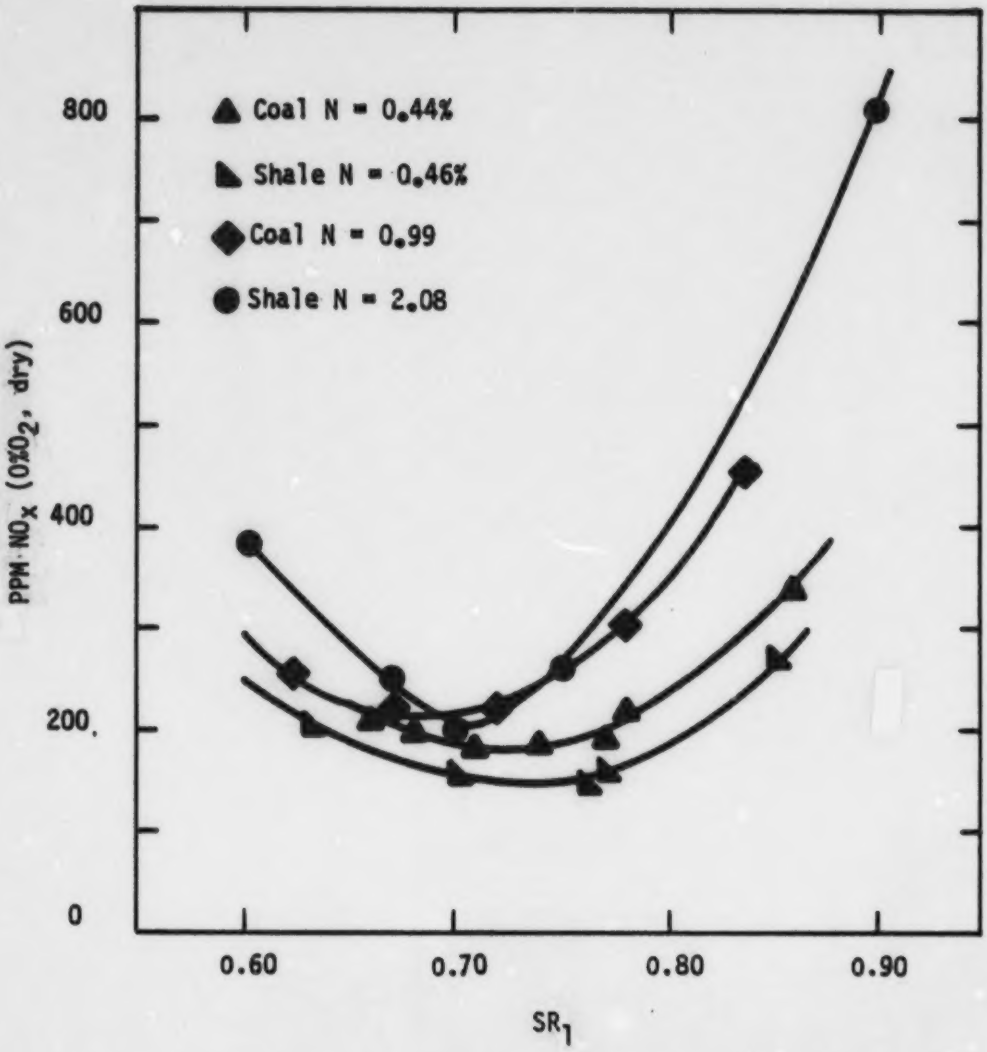

Figure 15. Minimum NO$_x$ Levels Achieved With Alternate Fuels (tunnel furnace primary zone residence time .83 sec).

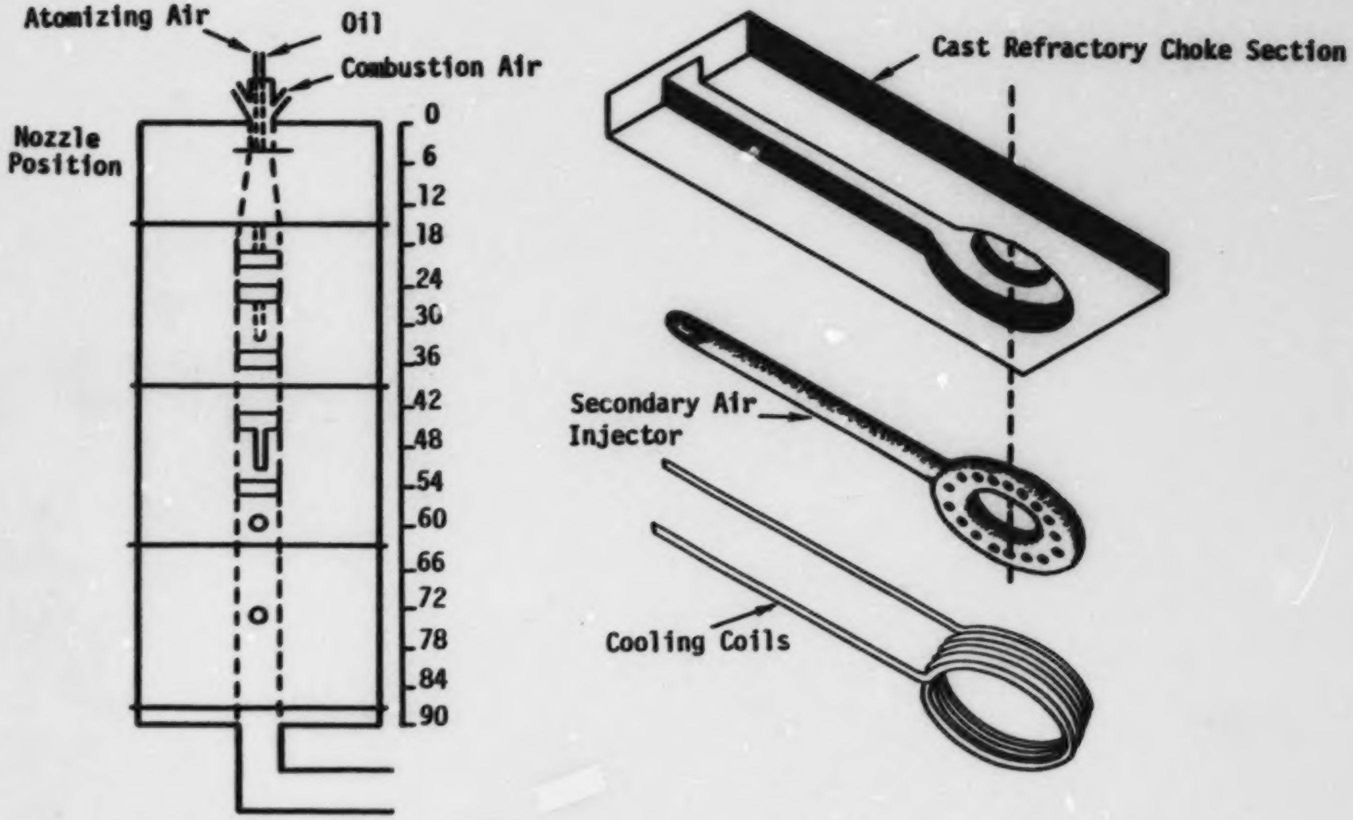
Atomizing Air
Oil
Combustion Air
Nozzle Position
0
6
12
18
24
30
36
42
48
54
60
66
72
78
84
90
Cast Refractory Choke Section
Secondary Air Injector
Cooling Coils

Figure 16. Modified Tunnel Furnace.

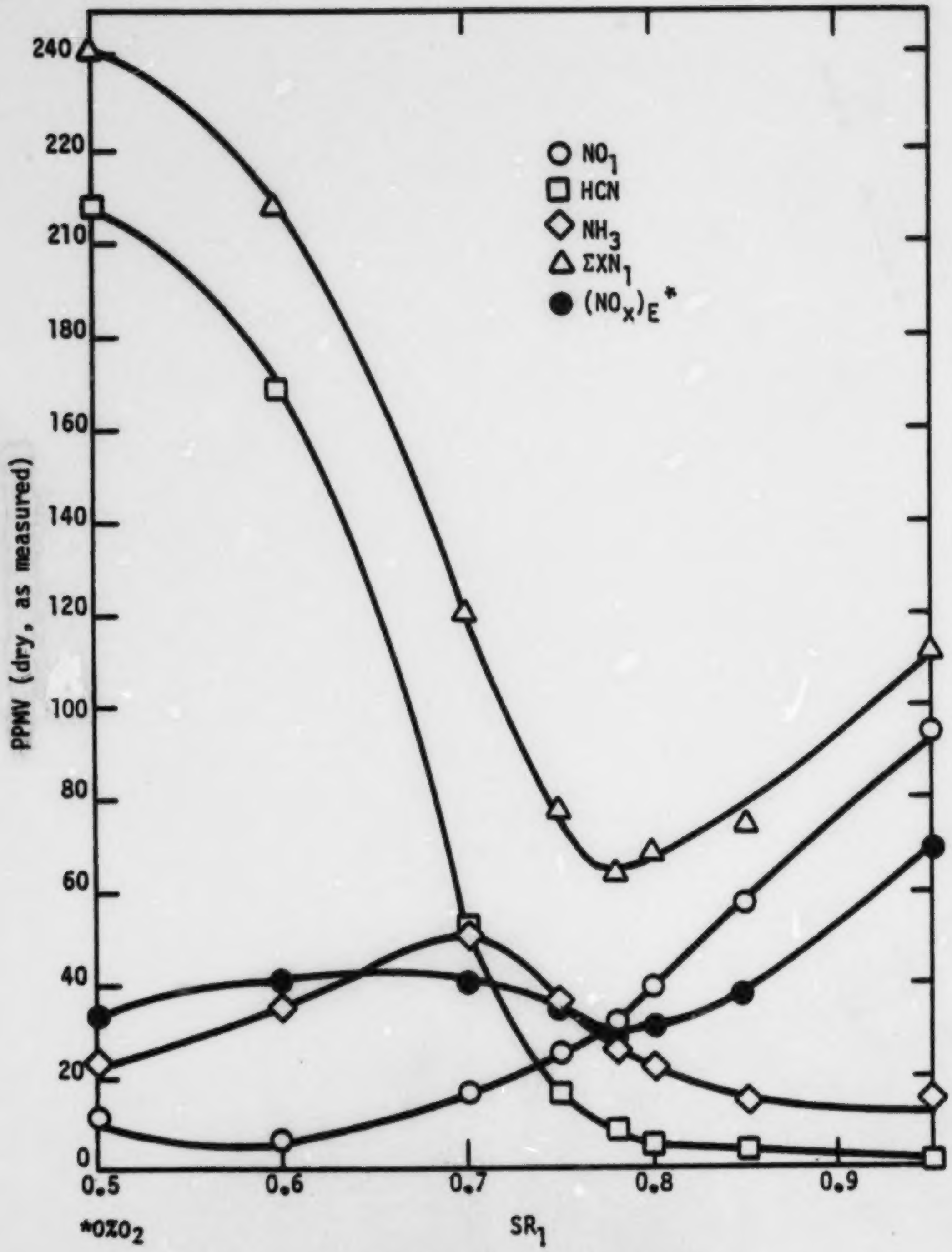

Figure 17. Detailed In-Flame Species Measurements With Alaskan Diesel Oil (D1).

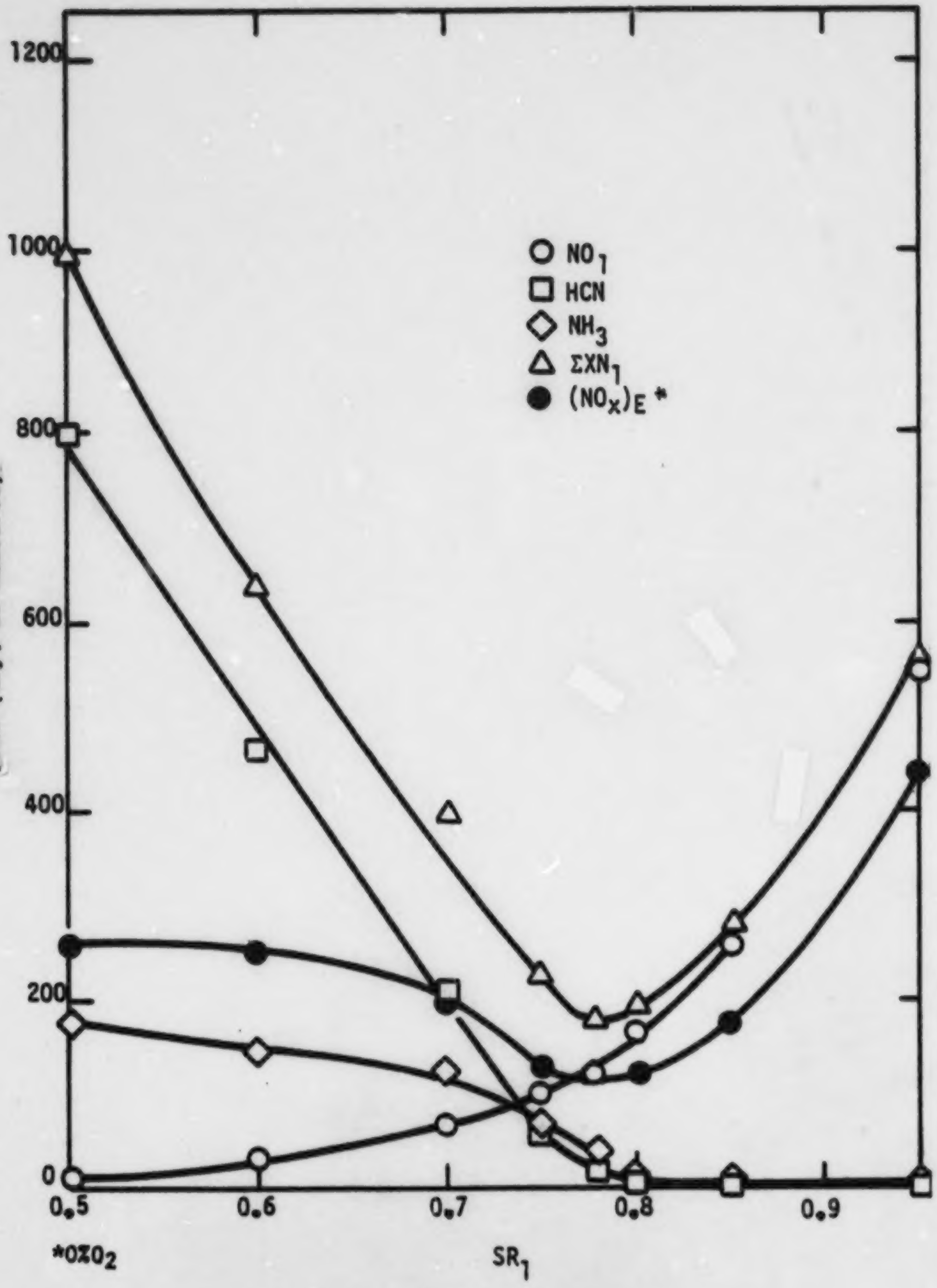

Figure 18. Detailed In-Flame Measurements With Kern County Crude Oil (R14).

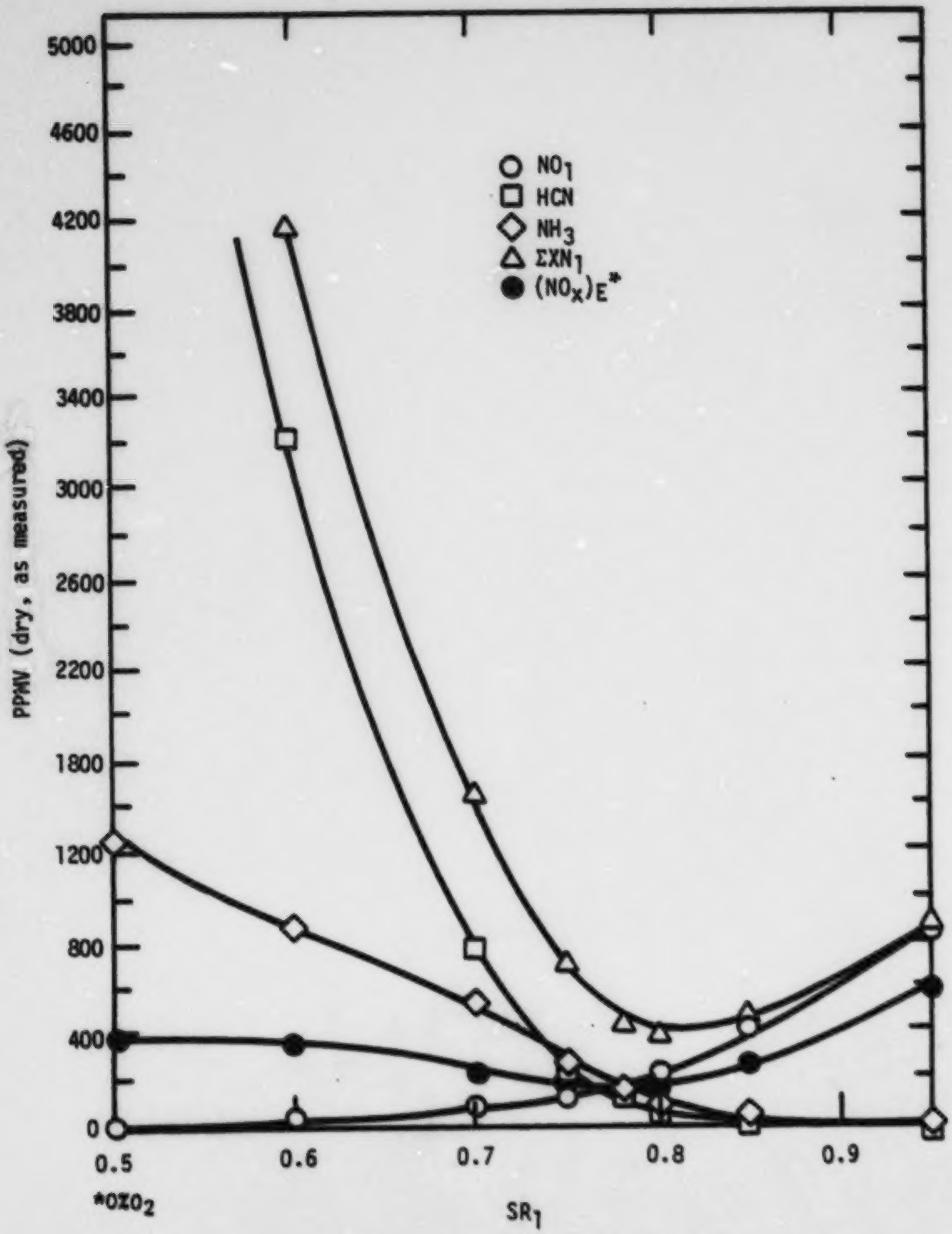

Figure 19. Detailed In-Flame Measurements With +850°F Shale Fraction (A8).

diesel), a high nitrogen residual oil (R-14-Kern County, California) and an alternative liquid fuel (A8-+850°F shale fraction). These measurements were made on the centerline of the furnace at a distance of 104 cm (approximately 630 msec) from the oil nozzle. Detailed radial measurements indicated that the concentration profile was essentially uniform at this location. All of the in-flame data are reported on a dry, as-measured basis. After each in-flame measurement, second-stage air was added at 107 cm and exhaust NO_x measurements were also made (shown on a dry, 0% O_2 basis). In general, decreasing the first-stage stoichiometric ratio reduced the NO concentration leaving the first stage. However, below a stoichiometric ratio of approximately 0.8 significant amounts of NH_3 and HCN were measured. Thus, there exists a minimum in exhaust NO_x concentrations because of a competition between decreased first-stage NO and increased oxidizable nitrogen species such as HCN. Figures 18 and 19 indicate that the petroleum-derived oil (0.83 percent N) and the heavy shale liquid (2.49 percent N) produce large amounts of HCN. In addition, both fuels exhibited a minimum in TFN at a first-stage stoichiometry of approximately 0.8.

Data for the Alaskan diesel oil (Figure 17) also show the presence of much smaller but significant concentrations of HCN and NH_3, although this fuel is essentially nitrogen-free. Total conversion of the fuel nitrogen would produce 21 ppm TFN at SR_1=0.7. This confirms previous work (10-12) which demonstrated that reactions involving hydrocarbon fragments and N_2 or NO can produce HCN.

Hydrocarbons

The rapid increase in HCN concentration below SR_1=0.8 was accompanied by an increase in hydrocarbon content of the partially oxidized combustion products. Figure 20 summarizes the in-flame hydrocarbon measurements for the Alaskan Diesel (D1), three petroleum-derived residual oils (Indonesian-R4, Alaskan-R9, Kern County-R14), three alternative liquids (SRC-II heavy distillate-A9, crude shale-A3, heavy shale fraction-A8) and methane containing 0.75 weight percent nitrogen as NH_3(⌀). Hydrocarbon concentrations correlate well on the basis of first-stage stoichiometry. At very low stoichiometric ratios the distillate oil (◆) and CH_4/NH_3 produced slightly higher hydrocarbon concentrations than the heavier liquid fuels.

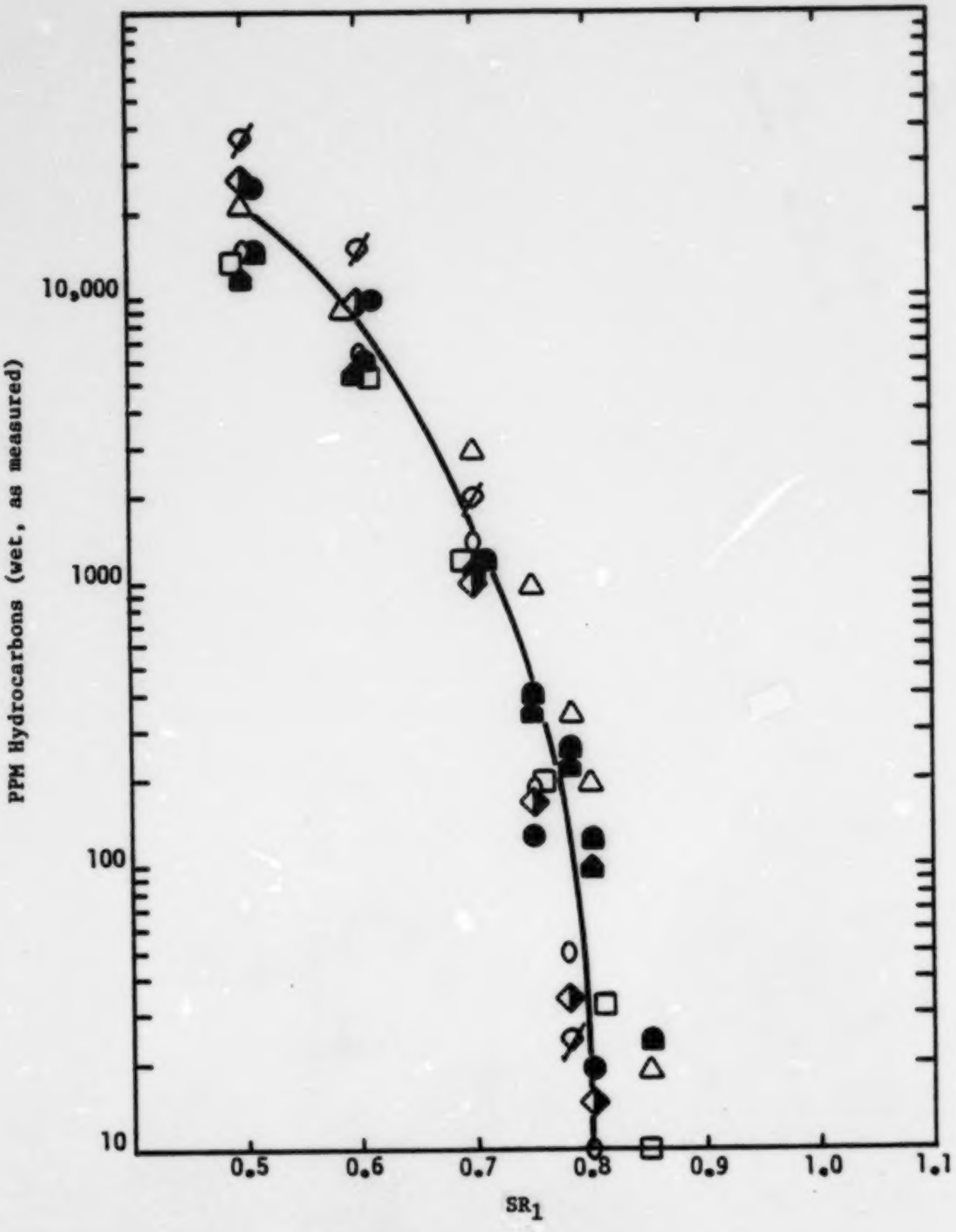

Figure 20. First-Stage Hydrocarbon Production.

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XN Distribution

Figure 21 shows typical results on the percentage of the original fuel nitrogen existing as either NO, NH_3 or HCN at various stoichiometric ratios for four fuels. Above $SR_1=0.8$, NO was the dominant TFN species; at lower stoichiometries HCN dominated with all fuels tested except the CH_4/NH_3. Axial profiles with the liquid fuels indicate that near $SR_1=0.8$, significant amounts of NH_3 may be formed early in the rich zone but they decay rapidly. These data are in strong contrast to similar results obtained with pulverized coal (20) which indicate that the preferred TFN species is a strong function of coal composition.

In general, both the alternate and petroleum-derived liquid fuels behaved very similarly with the exception of the Kern County, California crude (R14). It produced less HCN under rich conditions, and this tendency cannot be readily associated with common fuel properties. Hydrocarbon and nitrogen distillation data indicated that in terms of equilibrium volatile evolution the Kern County fuel is intermediate among the liquids tested. The Indonesian oil was the lightest of the liquid fuels and it produced the highest TFN concentration at the minimum ($SR_1=0.8$).

SECOND-STAGE NO_X FORMATION

Exhaust NO_x emissions in a staged combustor result from conversion of TFN exiting the first stage and any thermal NO_x production during burnout. Thermal NO_x production was not considered to be significant in this study because changes in heat extraction in the burnout region had almost no effect on final emissions. Figure 22 shows exhaust NO_x emissions as a function of total fixed nitrogen in the first stage at stoichiometries between 0.5 and 0.8 for all fuels. The form of this correlation can be compared with that presented in Figure 12 for excess air conditions since the second stage burnout can be considered an excess air flame. Exhaust emissions increase with increasing oxidizable nitrogen content, but the conversion efficiency decreases as the TFN concentration increases. There are three possible explanations for the data scatter shown in Figure 22: (1) TFN is not indicative of the oxidizable nitrogen compounds that are leaving the first stage; (2) TFN conversion in the burnout zone is dependent upon the form of the TFN;

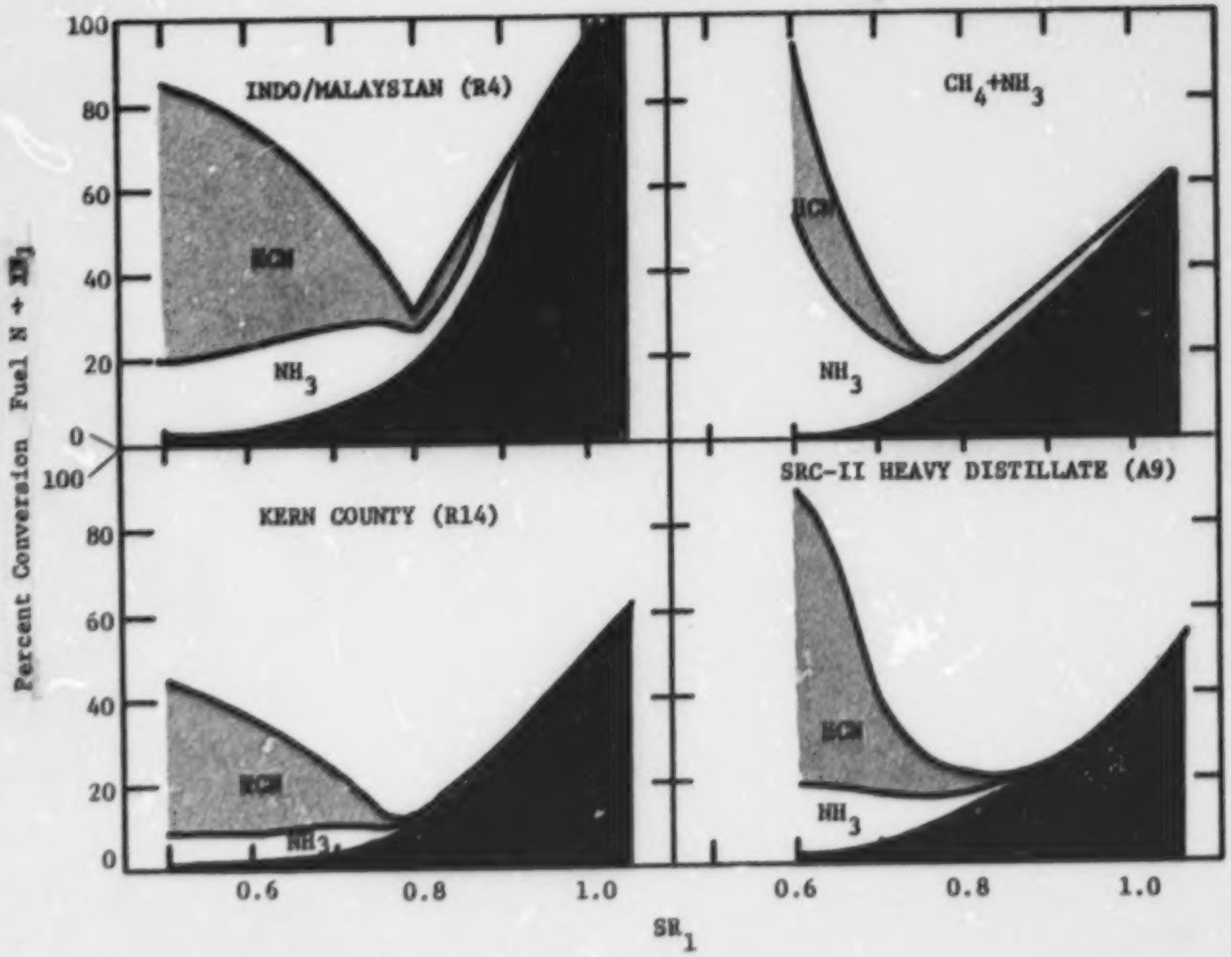


Figure 21. Distribution of First-Stage XN Species for Alternative and Petroleum-Derived Fuels.

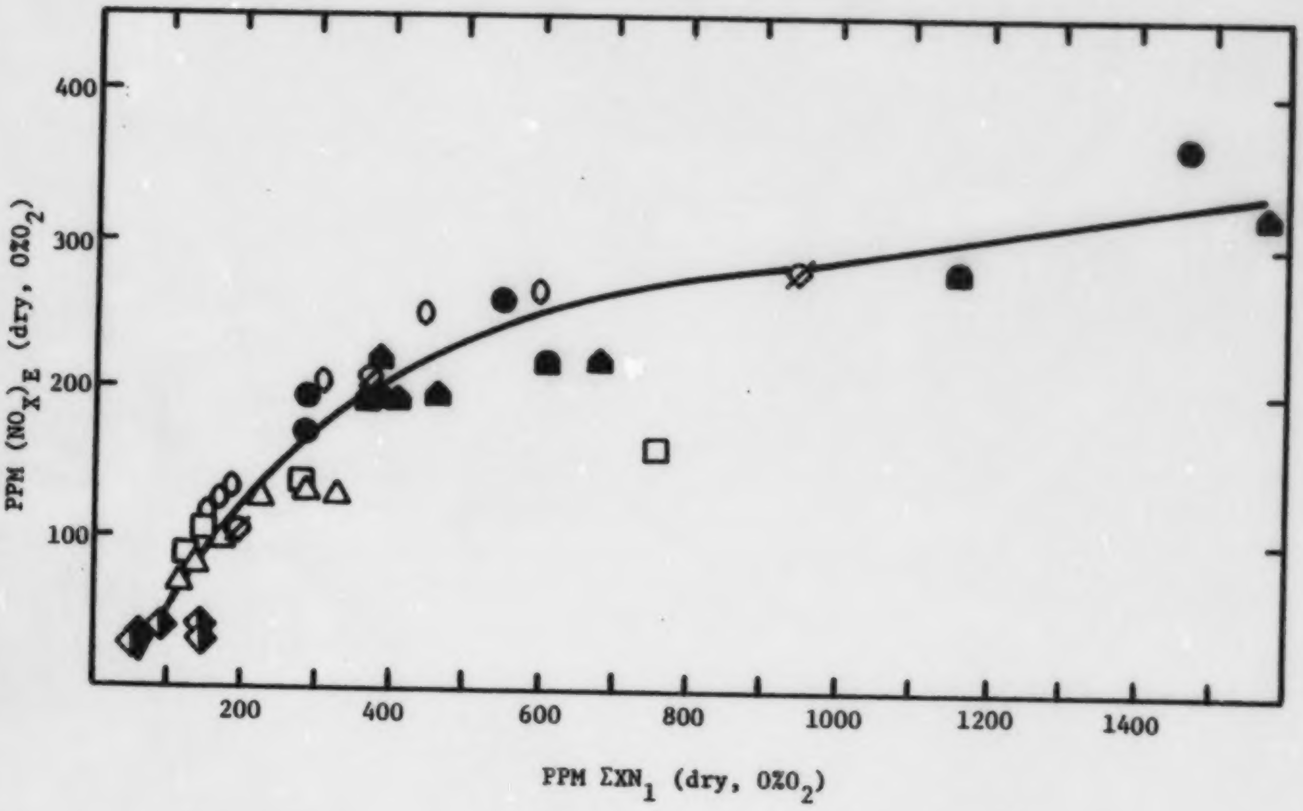


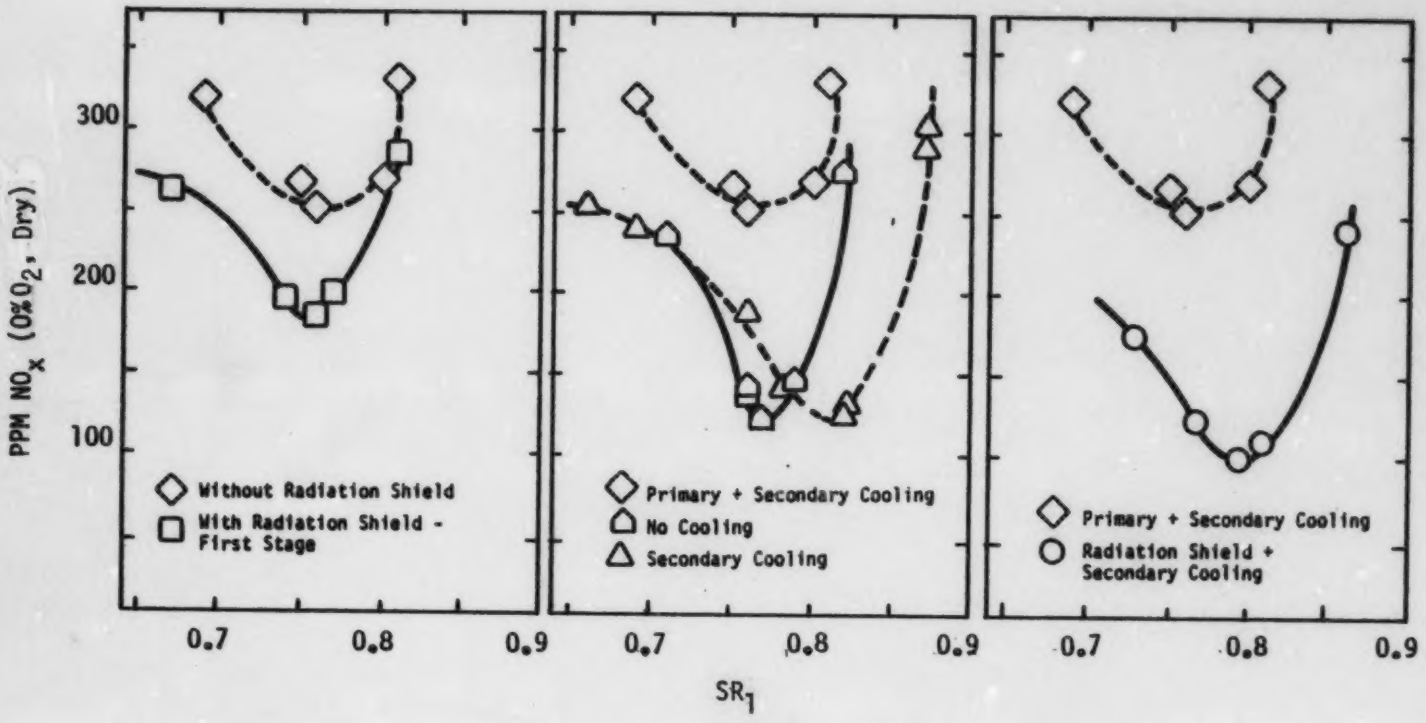
Figure 22. Exhaust NO_x Versus TFN at the Exit of the First Stage.

and (3) TFN conversion is also dependent upon the oxidation of the partial products of combustion at the exit of the fuel-rich zone.

IMPACT OF THERMAL ENVIRONMENT

The TFN concentrations shown in Figure 21 are in excess of equilibrium levels and Sarofim and co-workers (25) have suggested that increasing the temperature of the primary zone would prove beneficial. The results presented in Figure 23 were obtained with the shale crude (A3) to demonstrate the impact of first- and second-stage heat removal on the fate of fuel nitrogen. Figure 23a indicates that adding the radiation shield with cooling coils in both the first- and second-stage (hence, increasing the temperature of the vaporization zone) reduced the minimum NO_x emissions and shifted the optimum stoichiometry more fuel-rich. Figure 23b shows that removing the water cooling coils from the first stage reduced the exhaust emissions. Removing the second stage coils did not alter the minimum level; however, it did shift the minimum SR more fuel-rich. Thus, the optimum thermal environment has a high temperature vaporization zone, a hot, rich hold-up zone, and a cooled second stage (Figure 23c).

The axial profiles (22) provide an explanation for this shift in the minimum emission levels. Heat extraction in the first stage impacts the rate of decay of TFN. Under cold conditions, both NO and HCN essentially freeze, whereas without heat extraction the initial rate of decay for all three species is much faster leading to low TFN concentrations at the exit of the fuel-rich first stage. It should be noted that heat extraction also affects the rate of CO oxidation.



(a)

(b)

(c)

Figure 23. Influence of Heat Extraction Profile in the First and Second Stage Upon Exhaust NO_x Emissions.

SECTION 6

CONCLUSIONS

A rich/lean series staged combustor with a platinum/nickel oxide primary was the most promising low-NO_x combustor investigated with LBG. It had low conversions of fuel nitrogen to NO_x over a wide range of fuel-rich primary stoichiometries. Thus, it could be operated rich enough to maintain the adiabatic flame temperature relatively cool, prolonging the life of the catalyst. However, catalyst coated ceramics are often short-lived due to loss of activity of the coating and structural problems of the support caused by thermal shock. During the course of the bench-scale experiments there was a great change in the appearance of the Pt/NiO catalyst. A green coating formed on the surface. Also, the zirconia honeycombs became quite fragile after repeated thermal cycling, especially the fine-cell downstream monolith which was almost completely destroyed in the final experiments. Further investigation is necessary of catalyst aging and of pressure and throughput effects under optimized combustor conditions before a catalytic combustor could be considered a serious candidate for a gas turbine combustor.

A rich/lean series staged combustor with a diffusion flame primary also had low conversions of fuel nitrogen to NO_x. Primary stoichiometry and residence time had the most significant effects on fuel nitrogen conversion. Minimum NO_x emissions were achieved at primary stoichiometries around 90 percent theoretical air for long primary residence times (250 msec or longer). Pressure and Reynolds number had little effect on NO_x in a staged diffusion flame, while an increase in the hydrocarbon content of the LBG caused a slight increase in NO_x emissions. Combustion of a hydrocarbon-free LBG was not tested on the bench scale, but laboratory-scale tests indicated that the absence of hydrocarbons in the fuel could cause a significant reduction in NO_x emissions.

A lean unstaged diffusion flame produced higher NO_x emissions than the rich/lean staged diffusion flame. However, because of its simplicity, it remains an attractive low NO_x combustor concept. The influence of Reynolds number on NO_x levels in the lean flame suggests that NO_x emissions could be lowered by utilizing larger fuel tubes, perhaps approaching the levels achieved by the staged diffusion flame.

It is planned to investigate other combustor configurations including a premixed backmixed simulated stirred reactor and a combination diffusion flame/catalyst hybrid combustor. The zero dimensional stirred reactor is easy to model. It will provide experimental feedback for the fuel nitrogen processing kinetics code to be used in future prototype combustor design. The hybrid system will input low ΣXN containing fuel-rich diffusion-flame exhaust into a Pt/NiO cleanup catalyst prior to secondary burnout.

The results of the bench-scale studies on the influence of liquid fuel properties and thermal environment on NO_x formation indicate that:

- With liquid fuels, fuel nitrogen content is the primary composition variable affecting fuel NO formation. NO_x emissions increase with increasing fuel nitrogen. Alternative liquid fuels correlate with the high-nitrogen petroleum oils.
- Staged combustion dramatically reduces both fuel and thermal NO_x formation. Minimum emissions occur at a primary zone stoichiometric ratio between 0.75 and 0.85 depending on the combustion conditions.
- First-stage stoichiometry determines the dominant TFN species. Below SR_1=0.8 HCN is the dominant species, and above SR_1=0.8, NO is the dominant species. NH_3 concentrations at the first-stage exit generally accounted for less than 20 percent of the fuel nitrogen.
- Exhaust NO_x emissions are directly related to the TFN concentration at the first-stage exit. NO_x control for high-nitrogen fuels is most effective when a rich primary zone is held at an optimum stoichiometry to minimize the TFN concentration. This concentration is further minimized by increasing the temperature of the fuel-rich zone.

Figure 24 summarizes the impact of fuel-bound nitrogen content on minimum emissions observed under staged combustion conditions and the associated TFN. Under optimum staged conditions NO_x emissions (and TFN) correlate well with total fuel nitrogen content. Only the SRC-II heavy distillate (⬟) exhibited unusually high emissions and this was the direct result of a high TFN yield. These results suggest that NO_x emissions resulting from the combustion of coal- or shale-derived liquid fuels can be controlled in a cost-effective manner by modification to the combustion process. Low-NO_x combustors can be designed which are tolerant to wide ranges in fuel-bound nitrogen content. Thus, the production of alternate fuels should be optimized without regard for the reduction of fuel nitrogen content as a method of controlling NO_x emissions from stationary sources.

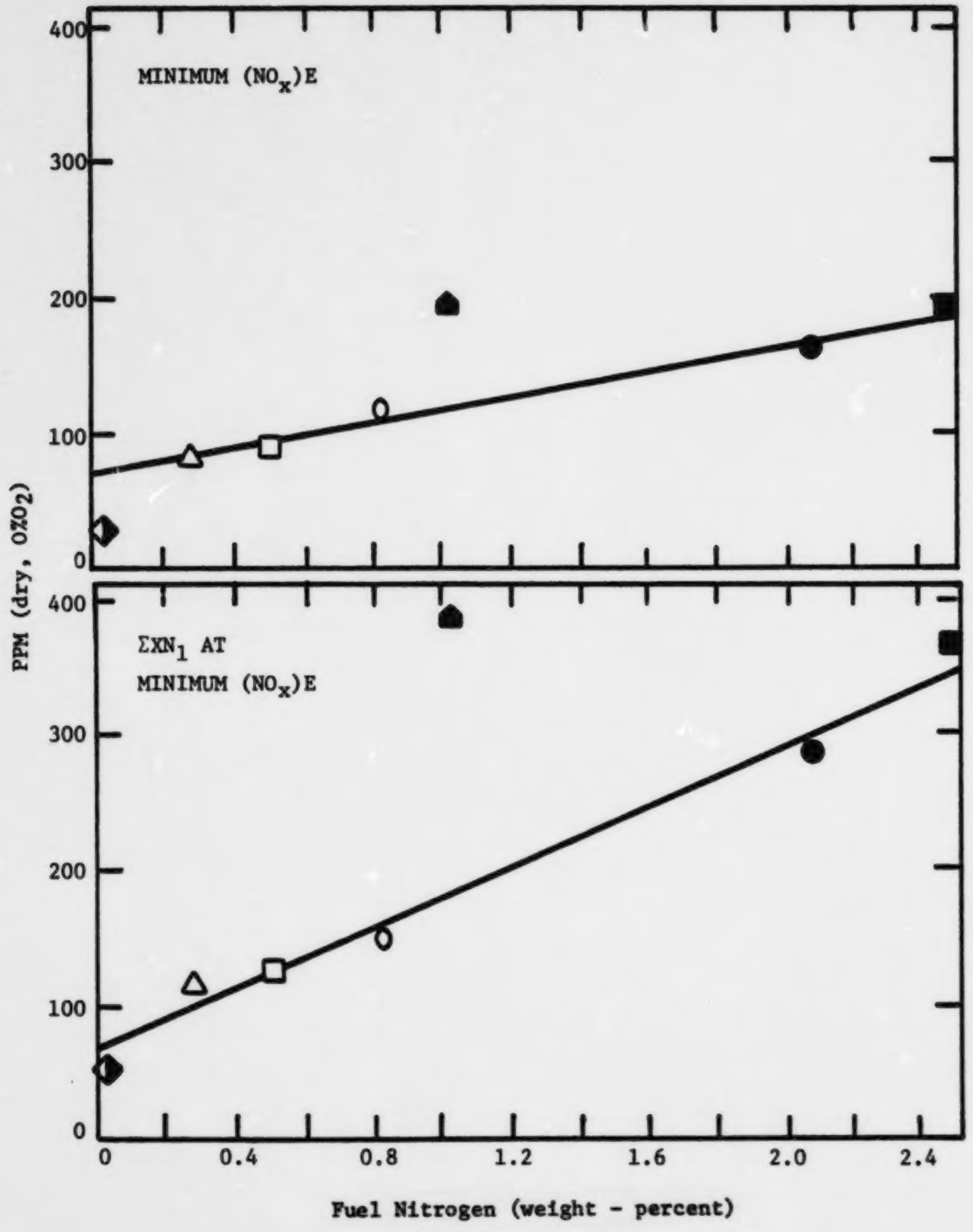


Figure 24. The Effect of Fuel-Bound Nitrogen Content on Exhaust NO_x and TFN in the Primary Zone (ΣXN_1) (SR_1 = 0.78, 3% overall excess O_2).

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PROBLEM-ORIENTED REPORT:

UTILIZATION OF SYNTHETIC FUELS: AN ENVIRONMENTAL PERSPECTIVE

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ABSTRACT

This paper discusses the potential environmental problems arising from the refining, transportation, storage and utilization of fuels produced by a synthetic fuels industry. Scenarios defining possible build-up rates for synfuel products from oil shale and coal conversion are developed to scope the magnitude of potential exposures. The market infrastructure for the use of these products is examined and the potential public health risks during the handling, transportation and utilization of these synfuel products is evaluated. Significant issues regarding environmental impacts and the need for regulatory attention are discussed.

PLANNING FOR SYNFUELS UTILIZATION MUST BEGIN NOW

This document is a preliminary overview intended to broadly sketch out the essential facts of interest to EPA about the utilization of synfuels and their potential environmental impacts. It is also intended to present an overall environmental perspective. A Final Environmental Market Analysis Report will be developed with the purpose of analyzing specific areas of relevance to EPA in greater depth and noting possible EPA activities for mitigating potential environmental impacts of synfuels.

EPA is currently sponsoring projects focussed on the environmental aspects of coal and shale conversion processes. This document deals more with the fate of synthetic fuel products after they leave the plant gate. Future work will be concerned in more detail with the estimated national flow rates and paths of such products and byproducts, their hazards to human health, and the risks of public exposure to these synthetic fuels.

In carrying out its mission of preserving the quality of our natural environment, EPA has the responsibility to keep fully abreast of synthetic fuel developments because a reasoned approach to dealing with the environmental impacts of a synfuels industry requires accurate knowledge about current synfuels processes and commercial applications.

Current trends in the international energy situation are rapidly increasing the probability that a domestic synthetic fuels industry will emerge in the 1980s. Because government incentives and private ventures in the synfuel arena are burgeoning in response to soaring world oil prices and decreasing reliability of oil imports, forecasters are now projecting earlier start dates, faster growth rates, and larger ultimate sizes for such an industry.

Several synfuel technologies are under consideration for commercial production. A wide range of synfuel products are expected to be produced and they will be utilized in a broad category of end uses (reference Table 1). Synfuels products will most likely be used largely as transportation fuel, including gasoline and diesel fuel from refined shale oil and coal conversion processes and jet fuel from refined shale oil. Utility and

Table 1. Synfuels Market Overview

WHAT TECHNOLOGIES PRODUCE SYNFUELS?		WHAT MAJOR PRODUCTS/ BYPRODUCTS WILL THEY MAKE?	WHERE WILL THE PRODUCTS/ BYPRODUCTS BE USED?	WHAT ARE THE RELATIVE POTENTIAL EXPOSURE LEVELS TO THE PRODUCTS?
OIL SHALE:	NUMEROUS RETORTING PROCESSES, INCLUDING TOSCO, PARAHO, UNION, OCCIDENTAL	Syncrude upgraded and refined to yield: LPG Gasoline Jet Fuel Diesel Fuel Residuals Lubricants[a] Waxes[a]	• Commercial and military transportation, including highway vehicles, aircraft, ships • Utility and industrial boilers • Commercial and residential heating • Industrial lubricants	Low for transport of crude shale to refinery; moderate during refining and end use as boiler fuel; increased exposure level when used in transportation sources and space heating.
DIRECT COAL LIQUEFACTION:	SRC-II	LPG Naphtha Fuel Oil SNG[b] Tar Oils[a]	• Utility and industrial boilers • Commercial and residential heating • Chemical feedstocks	Low for LPG, SNG, Naphtha, Butane; Moderate exposure for fuel oils at industrial sites with exposure increasing when used in space heating.
	EXXON DONOR SOLVENT	Propane Butane Naphtha Fuel Oil Solvent[a]	• Utility and industrial boilers • Commercial and residential heating • Paint thinners	
	H-COAL	Naphtha Fuel Oil	• Utility and industrial boilers • Commercial and residential heating	
INDIRECT COAL LIQUEFACTION:	FISCHER-TROPSCH	Gasoline LPG Diesel Fuel Heavy Fuel Oil Medium Btu Gas SNG Tar Oils[a] Phenols[a] Chemical Feedstocks[a] Pesticides[a] Fertilizers[a]	• Commercial and military transportation • Utility and industrial boilers • Commercial and residential heating • Chemical feedstocks • Agricultural uses	Low for LPG, SNG, and Medium Btu Gas. Moderate exposure when fuels used in transportation sources and boilers. Low to moderate exposure is also estimated when products used as chemical feedstocks.
	M-GASOLINE	Gasoline LPG	• Commercial and military transportation	
	METHANOL	Methyl Fuel Methanol	• Commercial and military transportation • Chemical feedstocks	
HIGH BTU COAL GASIFICATION:	NUMEROUS PROCESSES, INCLUDING LURGI, COED-COGAS, TEXACO, SHELL-KOPPERS	SNG[b]	• Commercial and residential heating	Very low - similar to current distribution of natural gas.
MEDIUM/LOW BTU COAL GASIFICATION:	NUMEROUS PROCESSES	Medium Btu Gas Low Btu Gas	• Captive fuel use for industrial heating and chemical feedstocks	Very low since it is primarily captive use.

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[a] Only representative byproducts are indicated.

[b] Substitute Natural Gas

industrial boilers will utilize the fuel oils produced from coal liquids. High-, medium-, and low-Btu gases from coal will find use in commercial, residential, and industrial heating applications. The products from most synfuel processes will be used as chemical feedstocks in a large variety of industries.

The national environmental impacts of a large-scale synfuels industry could be significant. The environmental concerns of end use, including handling and transport, will have to be investigated in detail. Since there is limited information concerning the end-use exposure effects of synthetic fuel products and by-products, the nature of these future impacts is largely speculative. In fact, since synthetic fuel technology is highly evolutionary, even the composition and amounts of future industrial synthetic fuel products and by-products are not well known.

In this report the term synfuel product refers to primary products of the synfuel industry such as gasoline, high-, medium-, and low-Btu gas, whereas the term by-product has been used to identify secondary useful products that are likely to be produced from synfuels such as plastics, solvents, varnishes, and fertilizers.

A SYNFUEL INDUSTRY IS EMERGING

INCENTIVES FOR SYNFUEL DEVELOPMENT ARE HERE

The primary incentive for synfuels development is the imbalance between domestic supply and demand for petroleum liquids and natural gas. The long-term decline in domestic oil production coupled with increased demand has resulted in a level of oil imports of 9 million barrels per day (MMBPD) of oil or about 50 percent of U.S. consumption. The proven domestic reserves of natural gas are also declining and demand is now being met with increasingly higher priced supplies.

A substantial market for liquid synthetic fuel products and chemical feedstocks is expected by 1990. A recent analysis concludes that about 2.9 Quads of energy or about 1.5 MMBPD will have to be supplied from synthetic liquid fuels (reference Table 2). As indicated in this analysis, use of synfuels is expected to be heavily directed toward transportation. Industry concern over potential interruptions in gas supplies has provided the incentive to develop coal gasification processes to supplement current gas supplies and for use as chemical feedstocks.

It is these considerations, along with the uncertainty inherent in the import supplies and the increasing problem of balance of payments, that now provide the impetus for Federal support for synfuels development. Recent Federal action creating the Synthetic Fuels Corporation (SFC) is aimed at alleviating some of the factors that to-date have discouraged development. The goal of the SFC, with authorized funds for loan guarantees, cooperative agreements, and price supports, is to reduce and share the investment risk of establishing a commercial synfuels industry.

Now, as the U.S. synfuels industry is a developing reality, the EPA will need to initiate close coordination with the SFC. As EPA takes the lead in regulatory approvals, other regulatory agencies will be encouraged to participate. A well organized, coordinated approach on the part of all Federal agencies will be viewed as an added incentive by the developing synfuels industry.

Table 2. Anticipated Liquid Fuel Products Demand in 1990[a/]

	Supplied to Consumers Quads	Petroleum Supplies Quads	Synfuels Quads
Gasoline	14.2	12.7	1.5
Jet Fuel	2.1	1.8	0.3
Kerosene	0.3	0.3	-
Heating Oils	6.4	5.7	0.7
Residual	3.2	3.2	-
Asphalt	1.0	1.0	-
Misc. Product	2.4	2.0	0.4
LPG	0.7	0.7	-
	30.3	27.4	2.9

a Coal Technology Market Analysis, ESCOE, January 1980. Assumes U.S. refineries will operate with the same mix as 1978.

b 1 Quad/yr = 0.5 MMBPD

SYNFUELS UNDER CONSIDERATION

The term "synfuels" has become synonymous with any combustible nonpetroleum fuel source which may include coal- and shale-derived fuels and feedstocks as well as those derived from agricultural products such as grain, wood, and cellulose. However, industry has become increasingly more interested in synfuel technologies with products that are easily substituted, in a marketing and utilization sense, for petroleum and natural gas. These synfuel technologies are those relating to coal- and shale-derived products. The following discussion is limited only to these products.

OIL SHALE RETORTING TECHNOLOGY IN HIGH GEAR

SHALE OIL MAY BE FIRST SYNFUEL TO ENTER THE MARKET AS A PETROLEUM REPLACEMENT

As a direct substitute for large volumes of liquid fuels, oil shale technology is perhaps closest to commercialization in the U.S.* Several consortia and companies with established shale oil projects have been engaged in the development of shale oil technology for some time. (reference Table 3). These projects are all located in prime shale areas of Colorado and Utah.

Many technologies are being developed and tested which are aimed at extracting kerogen, a waxy organic material, from shale. Most involve heating shale to about 480^{0}C and pyrolyzing the kerogen into a viscous liquid called shale oil. They differ in the manner in which this heating process is accomplished; surface retorting, in situ retorting, or modified in situ retorting.

In surface retorting, oil shale is mined, crushed to the proper size and then fed to a large kiln for heating. Several surface retorting processes are under development and they differ primarily in the heating method employed. Internal-combustion retorting heats shale by the circulation of hot gases that are produced inside the retort by the combustion of residual carbons in the shale. Gas-cycle retorts used by Union Oil heat the shale by circulating externally heated fluids. No combustion occurs inside the retort. In solid-heat-carrier retorting, shale is mixed with hot solids that are heated outside the retort and cycled through the shale. TOSCO II is an example of this method, using ceramic balls as the heat carrier.

In situ retorting pyrolyzes oil shale while it is still in the ground. The shale bed is ignited and sustained by injection wells, the shale is pyrolyzed, and the oil produced is pumped out of the retort volume through a production well. The spent shale remains in place. For successful in situ retorting, the shale bed must be made permeable to the flow of heat and product oil; various techniques of bed leaching or fracturing are employed. The difficulty of creating a permeable shale bed has led to the development of modified in situ processes. Vertical modified in situ

Table 3. U.S. Oil Shale Projects

Project	Location[1]	Technology	Production Capacity Goal (bbl/day)	Status
Chevron	Piceance Basin	Undecided	50,000	Technical assessment phase.
Colony (TOSCO, EXXON C)	Parachute Creek	Surface retorting	47,000	Construction of commercial modules scheduled for 1980.
Equity Oil	Piceance Creek	Solution injection, modified in-situ	-	Steam-injection feasibility
Geokinetics, Inc.	Uinta County	Horizontal modified in-situ	7-13 2,000-5,000	Several small retorts successfully burned; work on larger retorts in progress.
Getty Oil	Piceance Basin	Surface thermal extraction	-	Getty R&D proposal being considered by DOE
Mobil	Piceance Basin	Undecided	50,000	May start module in 1987
Occidental Oil	Logan Wash	Vertical modified in-situ	70,000	Six retorts burned; 48,000 bbl produced. Retorts 7 and 8 scheduled for cluster burn.
Occidental Oil - Tenneco	Tract C-b, Piceance Basin	Vertical modified in-situ	57,000	Shaft sinking in progress; construction of initial retorts scheduled for 1982.
Paraho (Development Engineering, Inc.)	Anvil Points	Surface retorting	150-200	Shut down due to lack of funding; 88,225 bbl produced over about one year period.
Rio Blanco (Gulf, Amoco)	Tract C-a, Piceance Basin	Vertical modified in-situ, surface retorting	50,000	Modular program consisting of 5 retorts scheduled for completion by 1982.
Superior Oil	Piceance Creek	Multimineral recovery, surface retorting	13,000	Company seeking land exchange with Federal Government which was denied in Febuary 1980.
TOSCO-Sand Wash	Uinta Basin	Modified in-situ, surface retorting	50,000	Feasibility studies in progress
Union Oil	Parachute Creek	Surface retorting	50,000	Construction of experimental mine and plant scheduled for 1982.
White River (Sohio, Sunoco, Phillips)	Tracts U-a and U-b, Uinta Basin	Modified in-situ, surface retorting	100,000	Operations suspended due to legal proceedings on ownership of lands.

[1] State Locations: Piceance Basin - Colorado; Parachute Creek - Colorado; Uinta County - Utah; Logan Wash - Colorado; Anvil Points - Colorado.

(VMIS) retorting removes a portion of the shale from the bottom of the deposit and fractures the remaining shale to create a chimney of shale rubble. The shale is retorted in this chimney from top to bottom. Occidental Oil Company has been testing VMIS retorting on shales at Logan Wash and Piceance Creek Basin in Colorado. Horizontal modified in situ retorting lifts the overburden in some cases, and fractures the shale seam to retort the shale from side to side. Geokinetics, Inc. is developing this technique in Utah.

The technology for surface retorting is more advanced than in situ retorting. Process variables are easier to monitor and control in above ground retorts than in underground retorts. However, large-scale commercial surface retorting requires large-scale oil shale mining, hauling, and crushing; and large-scale disposal of spent shale. It is also limited to that portion of the shale resources that is mineable. In situ retorting without mining is applicable to a greater variety of shale beds, and eliminates the requirements for handling, crushing, and spent shale disposal. Attempts to demonstrate this technology have identified many development problems. Modified in situ processes present a compromise, requiring some mining and handling, but offering more process control and easier development.

The crude shale oil produced by retorting will be upgraded by further processing. This upgraded shale oil, or syncrude, will be used as a refinery feedstock or boiler fuel. It is well suited for refining into middle distillate fuels. If hydrocracking is chosen for the refining process, the yield and range of products is particularly desirable: motor gasoline - 17 percent; jet fuel - 20 percent; diesel fuel - 54 percent; and residuals - 9 percent.

Several oil shale projects, with identified participants, plan to begin operation during the 1980s. The technologies, which are proprietary in many cases, appear to be sufficiently mature to move ahead to commercialization. Several retorts have been successfully operated by Geokinetics, Inc., Occidental Oil, Paraho, Union, and TOSCO. Colony, Union Oil, and Occidental Oil have announced plans to begin commercial development in 1980. All technologies have been demonstrated at pilot scale or larger.

BOTH DIRECT AND INDIRECT ROUTES TO COAL LIQUIDS ARE AVAILABLE

DEMONSTRATION AND FULL-SCALE UNITS ARE BEING ENGINEERED

Coal, hydrogen, and a coal-derived oil are mixed at high temperature and pressure to accomplish direct liquefaction. Under these conditions, the coal decomposes, and the fragments react with hydrogen to form additional derived oil, which is separated from the unreacted solids and further refined to produce usable liquid fuels. Indirect liquefaction processes react the coal with oxygen and steam in a gasifier to produce a synthesis gas composed mainly of carbon monoxide, carbon dioxide, and hydrogen. After the carbon dioxide and other impurities are removed from the gas, the carbon monoxide and hydrogen are chemically combined in a catalytic reactor to produce liquid products for use as chemical feedstocks or liquid fuels.

There are three major direct coal liquefaction processes currently undergoing development: SRC II, Exxon Donor Solvent (EDS), and H-Coal (reference Table 4). These processes differ mainly in the manner in which the hydrogen is made to react with coal fragments to produce the unrefined coal liquids. In the SRC II process, the coal feed and hydrogen are mixed with a process recycle stream that contains unreacted coal ash as well as coal-derived oil. The iron pyrite in the unreacted ash catalyzes the reaction between the coal fragments and hydrogen. In the EDS process, the coal feed and hydrogen are mixed with a specially hydrogenated coal oil called the donor solvent. The hydrogen added to the coal fragments is provided by the solvent and the hydrogen gas mixed in the reactor. The donor solvent is made by catalytically hydrogenating coal-derived oil using conventional petroleum refinery hydrotreating technology. In the H-Coal process, the unreacted coal and hydrogen are mixed with coal-derived oil and an added solid catalyst in a special reactor referred to as an ebullated bed.

Once the gases and distillable liquid products have been separated from the reactor effluent, the remaining "bottoms" material is processed. This material contains significant quantities of heavy hydrocarbons which must be efficiently utilized to enhance process economics. The principal bottoms processing step under consideration for the EDS process is

Table 4. Major Coal Liquefaction Processes

PROCESS	PROCESS TYPE	PRODUCTS	STATUS
Solvent Refined Coal, SRC II (Gulf Oil)	Direct liquefaction by solvent extraction: coal dissolved in solvent, slurry recycled, catalytic hydrogenation	LPG Naphtha Fuel Oil SNG	Pilot Plant under operation. 6700 ton/day of coal (20,000 barrels/day of oil equivalent) demonstration module under design and schedule for operation in 1984-1985
H-Coal (Hydrocarbon Research, Inc.)	Direct liquefaction by catalytic hydrogenation, ebullated catalyst bed	Naphtha Fuel Oil	600 ton/day (1400 barrels/day of oil equivalent) pilot plant under construction, testing will begin in 1980. Plant is located at Catlettsburg, Kentucky
Exxon Donor Solvent, EDS (Exxon Research and Engineering Company)	Direct liquefaction by extraction and catalytic hydrogenation of recycled donor solvent	Propane Butane Butane Naphtha Fuel Oil	250 ton/day (500 barrels/day of oil equivalent) pilot plant under construction, testing will begin in 1980. Plant is located at Baytown, Texas
Fischer-Tropsch (M.W. Kellogg/Lurgi)	Indirect liquefaction, liquefaction of synthesis gas in an fluid bed catalytic converter	Gasoline LPG Diesel Fuel Heavy Fuel Oil Medium Btu Gas SNG	SASOL I, 800 tons/day, producing over 10,000 bbl day of liquids in commercial production since 1956. SASOL II, 40,000 tons/day, producing over 50,000 bbl day of liquids has been completed and will begin start-up in 1980. SASOL III with approximately the same capacity as SASOL II is currently being planned.
Mobil M	Indirect liquefaction, liquefaction of synthesis gas in fixed bed using molecular size-specific zeolite catalyst	Gasoline LPG	Commercial scale plant to produce 12,500 barrels of gasoline using reformed natural gas is planned for New Zealand in 1984-1985

FLEXICOKING, which consists of thermal cracking of the bottoms to produce additional liquids and coke. The coke is subsequently gasified to produce plant fuel gas or hydrogen for the liquefaction step. Bottoms processing for the SRC II and H-Coal processes probably will be partial oxidation (i.e., gasification) to produce hydrogen for the liquefaction step.

There are two major indirect coal liquefaction processes: Fischer-Tropsch which is commercial now in South Africa, and Mobil-M which is expected to be commercial in 1983-84. In the Fischer-Tropsch process, the purified synthesis gas from the gasifier is reacted over an iron catalyst to produce a broad range of products extending from lightweight gases to heavy fuel oil. The broad product distribution from this process is generally considered as a disadvantage where large yields of gasoline are desired. Improved catalysts are currently being developed at the bench scale to maximize the yield of gasoline-range hydrocarbons. In the Mobil-M process, the synthesis gas is first converted to methanol using commercially available technology. The methanol is then catalytically converted to high-octane gasoline over a molecular-size-specific zeolite catalyst.

Indirect coal liquefaction is successfully operating on a commercial scale at the SASOL I plant in South Africa using the Fischer-Tropsch technology. The SASOL I plant produces gasoline, jet fuel, diesel oil, middle distillates, and heavy oil. SASOL II, producing 50,000 barrels per day of coal-derived liquids, has been completed and will begin operation later in 1980. Active interest in this technology has developed and plans to license and construct similar plants in the U.S. are progressing. There is strong interest in the Mobil-M gasoline indirect process because of its attractive high-octane gasoline yield. A commercial-scale plant producing 12,500 barrels per day of gasoline is planned for operation in New Zealand by 1985.

Direct coal liquefaction technologies are in various stages of development. SRC I and II processes have been tested at the pilot plant level and are entering into the demonstration plant stage.

Large pilot plants are currently under construction for testing of the H-Coal and EDS processes. These plants are located at Catlettsburg, Kentucky, and Baytown, Texas, respectively.

SRC I process produces primarily a solid product with a small amount of useful liquid product. However, SRC II process produces primarily liquid products.

In addition to these major coal liquefaction technologies, several other processes have received attention, including the Dow process, Riser Cracking, Synthoil, and the Zinc Halide process. All have been tested in small-scale units.

A WIDE VARIETY OF COAL MAY BE USED IN THE SYNFUELS INDUSTRY

Most coal gasifiers react coal, steam, and oxygen to produce a gas containing carbon monoxide, carbon dioxide, and hydrogen. When air is used as the oxygen source, the product gas contains up to 50 percent nitrogen and is referred to as low Btu gas since its heat of combustion is only 80 to 150 Btu/standard cubic feet (scf). Synthesis gas or medium-Btu gas ranges from 300 to 500 Btu/scf.

Low-Btu gas is used as a fuel gas near its point of generation since its low heating value makes it uneconomical to distribute over long distances. Medium-Btu gas can be used as a fuel gas and transported economically over distances of up to 200 miles. It can also be used as a chemical feedstock for the production of methanol or gasoline. Finally, it can be converted catalytically to substitute natural gas (SNG), having a heating value of about 1,000 Btu/scf. Additionally, medium-Btu gasification is an integral part of all indirect liquefaction technologies.

There are many coal gasification technologies that differ in design and operation, depending upon the type of coal used and the product desired. High- and medium-Btu gasification technologies using noncaking coals characteristic of U.S. western coals are relatively well developed. Severe operational problems are encountered with commercially available gasifiers in processing caking coal such as those found in the eastern U.S. Several gasification technologies for high- and medium-Btu gases are under active development (reference Table 5). Many additional processes are being tested, but at less advanced stages of development (reference Table 6).

A fixed-bed gasifier, such as the Lurgi, feeds coal to the top of the gasifier. The descending coal is successively dried, devolatilized, and gasified in contact with gases rising from the bottom. Steam and oxygen are introduced at the bottom of the gasifier, and solid ash is removed through an ash lock. In some gasifiers, such as British Gas Company (BGC) Lurgi, the temperature at the bottom of the bed is sufficient to melt the

Table 5. Coal Gasifiers for High, Medium and Low Btu Gas

Process	Process Type	Potential Products	Most Suitable Products	Status
Lurgi Dry Ash	Pressurized fixed bed, dry bottom	Substitute Natural Gas (SNG, also known as High Btu Gas), Medium Btu Fuel[a] Gas, Low Btu Fuel Gas	SNG, Medium Btu Fuel Gas, Low Btu Fuel Gas	40 years of commercial development and 14 commercial plants located in Australia, Germany, UK, India, Pakistan, South Africa, Korea. Average module size 800 tons/day (2000 BOE)[c]
British Gas Company (BGC) Lurgi	Pressurized Fixed bed slagging bottom	SNG, Medium Btu Fuel Gas, Low Btu Fuel Gas	SNG, Medium Btu Fuel Gas, Low Btu Fuel Gas	790 tons/day (of coal) (2000 BOE) pilot plant tested in Westfield, Scotland
Texaco	Pressurized single stage entrained, slurry feed	SNG, Medium Btu Synthesis Gas, Low Btu Fuel Gas	Medium Btu Synthesis[b] Gas	160 ton/day (400 BOE) plant operating in West Germany
U-Gas Institute of Gas Technology (IGT)	Pressurized fluid bed, ash agglomerating	SNG, Medium Btu Fuel Gas, low Btu Fuel Gas	Medium Btu Fuel Gas	14000 tons/day of coal plant (35000 BOE) producing Medium Btu Fuel Gas, under design for construction in Tennessee
Westinghouse	Pressurized single stage fluid bed, ash agglomerating	SNG, Medium Btu Fuel Gas, Low Btu Fuel Gas	SNG, Medium Btu Fuel Gas	15 ton/day (40 BOE) process development unit, under testing at Waltz Mill, Pa.
Shell Koppers	Pressurized entrained, dry feed	Medium Btu Synthesis Gas, Low Btu Fuel Gas	Medium Btu Synthesis Gas	150 ton/day (400 BOE) pilot plant in operation in W. Germany. 1,000 ton/day scheduled in 1983/1984.
Koppers-Totzek	Atmospheric entrained, dry feed	Medium Btu Synthesis Gas, Low Btu Fuel Gas	Medium Btu Synthesis Gas	1,000 ton/day (2500 BOE) plant in operation in South Africa for the production of ammonia

[a] Medium Btu Gas with significant concentration of methane is more suitable for use as fuel, and therefore identified as Medium Btu Fuel Gas.

[b] Medium Btu Gas with low concentration of methane is more suitable for chemical synthesis,ard therefore identified as Medium Btu Synthesis Gas

[c] BOE - Barrels per day of oil equivalent

Table 6. Status of Other Coal Gasification Processes

DEMONSTRATION PLANTS	SCALE (tons/day coal feed)	STATUS
HYGAS	7340	Conceptual Design[a]
COED-COGAS	2210	Detailed Design[b]
U-GAS	3160	Detailed Design
PILOT PLANTS/PDUs		
BELL HIGH MASS FLUX	6	Operational[c]
BIGAS	120	Operational
COMBUSTION ENGINEERING	5	Operational
DOW	24	Under Construction
EXXON CATALYTIC	100	Proposed
GEGAS	24	Operational
HYDRANE	4	Proposed
MOLTEN SALT	24	Operational
MOUNTAIN FUEL	12	Proposed
SYNTHANE	72	Mothballed
TRI-GAS	1	Operational

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[a] Conceptual design incorporates all important details of major unit areas in the plant. Material balances are provided around all major unit areas. (Unit area is a section of the plant consisting of several components integrated to perform a single transformation on the product stream. Examples are gasification, raw gas cooling, gas cleanup, or methanation.)

[b] All equipment and detailed pipeline diagrams are prepared as part of detailed design. In addition, detailed material balances are prepared for each piece of equipment.

[c] The plant is either operating or has operated successfully in the past.

ash, allowing its removal as molten slag. The slagging feature provides a distinct advantage in contending with the caking characteristics of eastern U.S. coals.

Lurgi high-pressure operation, in conjunction with relatively low gasification temperatures, favors the formation of significant quantities of methane in the gasifier, enhancing the heating value of the product. These conditions also favor production of by-products such as tars and impurities like phenols, organic nitrogen compounds, and sulfur compounds.

In fluid-bed gasifiers currently under development, high-velocity gases pass up through the bed to fluidize the coal, providing excellent mixing and temperature uniformity throughout the reactor. Operability with caking coals (eastern U.S.), as well as low tar production and tolerance to upsets in fuel rates, has been demonstrated at the pilot scale for both the Westinghouse and U-Gas gasifiers.

The Texaco and Koppers-Totzek gasifiers are representative of entrained-bed technology in which the solid particles are concurrently entrained in the gaseous flow. Flame temperatures at the burner discharges are in the range of 1370 to 1925°C, resulting in melting of the coal ash with minimum production of impurities. Entrained-flow gasifiers may be favored for the production of synthesis gas for indirect liquefaction. They can operate with caking coals. However, compared to fluid-bed gasifiers, they have very low carbon holdup capability in the reactor and, therefore, have limited safeguard against possible formation of explosive mixture in the reactor in case of coal feed interruption.

There has been extensive commercial experience in the U.S. with low-Btu coal gasification technologies operating near atmospheric pressure. However, these applications have been limited to small-scale captive applications for providing industrial process heat and space heating. For example, the Wellman-Galusha gasifier designed for atmospheric pressure operation was used extensively by industry years before pipeline-supplied natural gas was readily available at comparatively lower cost. Pressurized gasification processes capable of yielding high-Btu gas for pipeline use and medium-Btu gas for chemical feedstocks are less developed, with the exception of the Lurgi fixed-bed process. The Lurgi process is based on 40 years of commercial development at 14 commercial plants that are located in

Australia, Germany, U.K., Korea, India, Pakistan, and South Africa. A great deal of interest in the Lurgi technology is emerging in the U.S. with several announced plans for SNG production by pipeline and gas utility companies. Several projects utilizing the Texaco process for captive applications (chemical feedstocks and on-site power generation) are in the planning and design stage with at least one project (Tennessee-Eastman) scheduled for construction in 1980.

DEVELOPMENT OF THE SYNFUELS INDUSTRY OVER THE NEXT 20 YEARS

Three scenarios or projections of synfuel industry buildup rates to the year 2000 have been developed to illustrate the potential range of synfuel product utilization:

- A "National Goal" scenario driven by Federal incentives
- A "nominal production" or most likely scenario
- An "accelerated production" scenario representing an upper bound for industry buildup.

ACHIEVING THE NATIONAL GOAL - SCENARIO I

In July 1979, President Carter announced new energy initiatives for the U.S. aimed at reducing our dependence on imported oil. One of the key elements of this policy is the provision of Federal funds to stimulate production of synthetic fuels at the rate of 2.2 million barrels per day (MMBPD) by 1992. Specifically, the national synfuel goals are:

Coal Liquids. To stimulate and accelerate the construction and operation of the first few plants to provide sufficient data on the competing commercial coal liquefaction processes so that industry, with its own investment, stimulated by Government incentives if required, will build plants with sufficient capacity to provide upwards to 1 MMBPD liquid fuels by the year 1992.

Shale oil. To stimulate shale oil production at the rate of 0.4 MMBPD by 1990.

High-Btu Gas. To develop and implement a program that enables the U.S., by 1992, to produce significant quantities of pipeline quality gas (0.5 MMBPD - oil equivalent*) from commercial HBG plants in an environmentally acceptable manner. This is facilitated by the short-range goal of having two or three commercial HBG plants in operation by the mid-1980s.

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*For easy comparison with petroleum supply/demand figures, synfuel production rates are expressed in barrels of oil equivalent in this document. This does not imply that high-, medium- and low-Btu gases from coal that are substituted for domestic natural gas will have any direct effect on the reduction of imported oil.

Low-/Medium-Btu Gas. To stimulate an initial near-term commercial capability for several medium-Btu commercial plants in key industries as well as utilities, for energy and feedstock applications for both single and multiplant use, and for multiple applications of low-Btu gas in each of the prime industry markets. Commercial-scale development will depend on the long-term economics of this technology, vis-a-vis the price of domestic oil and natural gas. Once a capability has been established, capacity will be accelerated to achieve at least 0.29 MMBPD oil equivalent by 1992. Of this total, up to 0.04 MMBPD oil equivalent will be provided from 40 to 50 low-Btu facilities and up to 0.25 MMBPD oil equivalent from 25 to 30 medium-Btu plants. Again, it must be mentioned, that if this low- and medium-Btu coal-gas is substituted for natural gas, there will not be a direct effect on the reduction of imported oil.

The key assumptions allowing achievement of these goals are: (1) Federal funds provided are sufficient to reduce investment risk by the synfuel industry through 1992, and (2) other requirements for industry development are satisfied, i.e., environmental permits, material, equipment, and labor. A likely buildup rate profile for the synfuel industries under this scenario is shown in Figure 1.

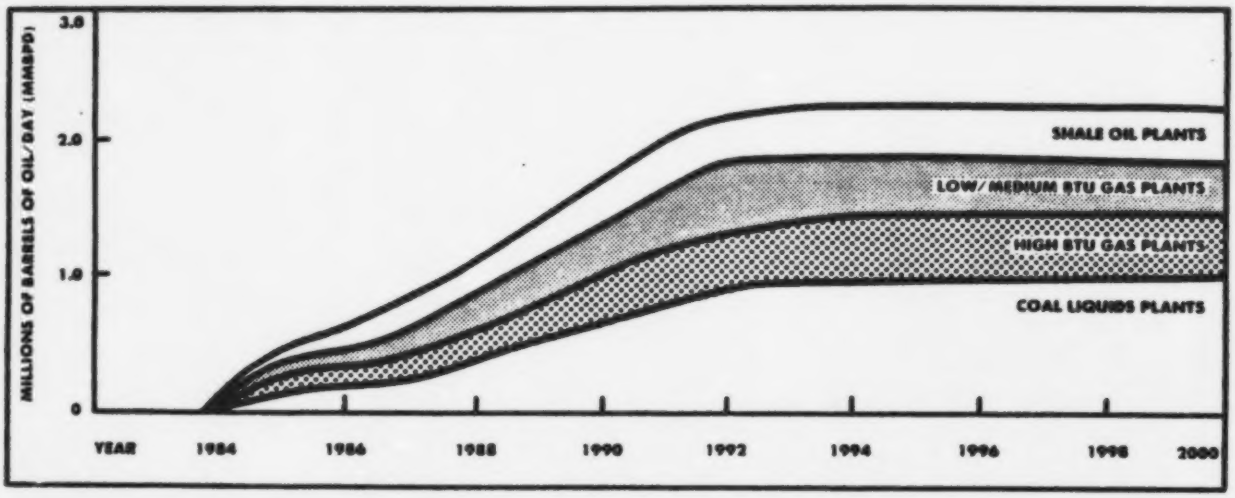


Figure 1. Synfuels Industry Buildup for the National Goal Scenario

For shale oil, several of the most advanced projects were selected as a basis. The planned operation startup schedules and capacity buildup rates for these projects were used to generate the industry production buildup profile to about 0.4 MMBPD by 1992. The period beyond 1992 is viewed as one of technology consolidation: gaining a firm footing with regard to environmental and economic performance and technology improvements. This type of industry production profile is not without precedent; for example, the Federal support of the synthetic rubber industry during World War II.

The goal of 1 MMBPD of coal liquids will be met predominantly by indirect coal liquefaction. At present, the only commercially demonstrated coal liquefaction process is the Fischer-Tropsch embodied in the SASOL plants in South Africa. The Mobil-M process should be commercially demonstrated within the next five years. Considering construction and permitting lead times, plants of this type could begin operation around 1985. To meet the production goal, 10 to 15 plants of a nominal 0.05 MMBPD capacity must be in operation by 1992. A potential drawback to the commercialization of SASOL technology in the U.S. is the broad product distribution, ranging from light hydrocarbon gases to heavy fuel oil. The Mobil-M technology, on the other hand, produces an all-gasoline product which would be particularly well suited to the U.S. market demands. Given this apparent advantage of Mobil-M technology over SASOL, it is believed that industry should favor commercialization of both Mobil-M and SASOL technology during the next few years, with the breakdown being roughly 50/50. Approximately 75 percent of the coal liquids production will be due to these indirect liquefaction processes.

For the direct liquefaction processes, there will not be sufficient experience and information to attract any more than developmental interest over the next few years, under this scenario, By 1985 there should be sufficient information available from the operation of the EDS, H-Coal and SRC II plants to support a commercialization decision concerning these processes. Federal incentives will likely be distributed such that by 1992, three or four pioneer commercial-scale plants employing direct liquefaction will begin to appear. Of the total production goal of 1 MMBPD of coal liquids it is estimated that 25 percent will be produced by these first commercial direct liquefaction plants embodying the basic SRC II, EDS and H-Coal technologies, or improvements and modifications to these. It is projected that for the next few years after 1992, production will remain at 1 MMBPD while technological evaluations are performed. These direct liquefaction plants will be located near the major eastern U.S. coal areas.

The Lurgi fixed-bed process is the lead high-Btu coal gasification technology and has been commercially demonstrated outside the U.S. It is expected to be utilized in all commercial plants constructed over the next 10 years. As the process requires noncaking coals, these plants will most likely be located in the western U.S. Interest will continue in other high-Btu gasification technologies such as the Slagging Lurgi which is capable of using eastern caking coals. At least one of these alternate or advanced processes probably will be supported under Federal incentives but it is unlikely that a commercial plant will appear until the early 1990s, and this would probably be located near a midwestern coal resource.

The Lurgi fixed-bed medium-Btu process is the lead technology for medium-Btu gas. Texaco partial oxidation gasification or similar pressurized entrained-bed gasifiers such as pressurized Koppers-Totzek, will be under development and demonstration during the early 1980s and will likely serve as the prime medium-Btu gasification process for eastern coals. To 1992, however, the major buildup in medium-Btu gasification will come from Lurgi plants located in the western U.S.

For low-Btu gasification, the several technologies that are currently available and providing commercial service are assumed to be easily applied, under the incentives existing to 1992, to generate the 0.04 MMBPD production rate goal. Low-Btu gas will generally be captively employed as fuel gas or used on-site for combined-cycle power generation.

The production buildup profile for major synfuel products resulting from of the synfuels industry buildup in Scenario I is shown in Figure 2. These product quantities are projected to enter commercial use and are to be considered in assessments of potential environmental impacts from synfuels. Naturally, these major products are presented for the sake of clarity, but there are many other products and byproducts that will be produced and distributed into the market place. These products and byproducts will also vary in greater or lesser quantities in Scenarios II and III which follow.

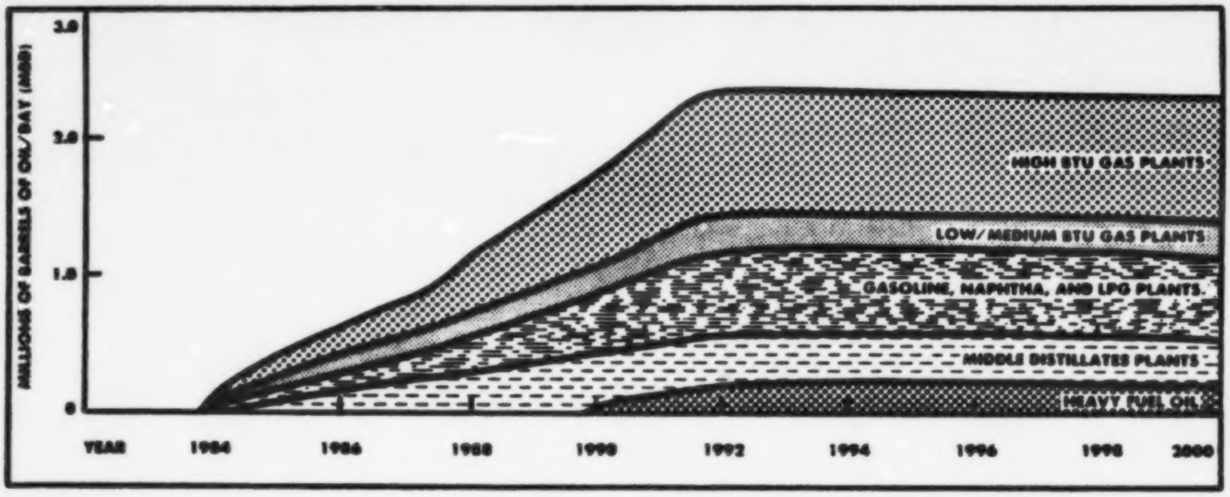


Figure 2. Major Synfuel Product Buildup for the National Goal Scenario

PRODUCTION AT A NOMINAL RATE - SCENARIO II

Recent studies of the technical capability of the U.S. to meet the synfuel national goal point out that there are significant concerns regarding achieving this goal. They include:

- Availability of skilled manpower: it is expected that the supply of engineers and construction labor will be severely taxed to meet the synfuel production goal set forth in Scenario I.
- Availability of critical equipment: certain critical equipment for the synfuel industry such as compressors, heat exchangers, and pressure vessels are expected to be in short supply unless corrective measures are taken now, thus slowing the synfuel industry buildup rate indicated in Scenario I.
- Diversion of investment to competing technologies: demand on the limited capital available in the economy by competing energy supply technologies, such as coal liquefaction, coal gasification, oil shale, geothermal, and solar technologies, could result in the slowing of buildup rates for some technologies.
- Environmental data: lack of environmental data needed for regulatory approvals could slow down the buildup rate.

- Licensing: time and construction schedule constraints imposed by State and Federal licensing and permitting requirements could hinder synfuel industry buildup rate.

Taking these concerns into consideration, a nominal synfuels production buildup - Scenario II - has been developed, as indicated in Figure 3. A production rate of about 2.1 MMBPD is estimated by the year 2000, instead of 1990 as indicated in Scenario I. The technologies expected to contribute to both Scenarios I and II are the same; the major difference is in the rate of buildup: it is slower and delayed in time.

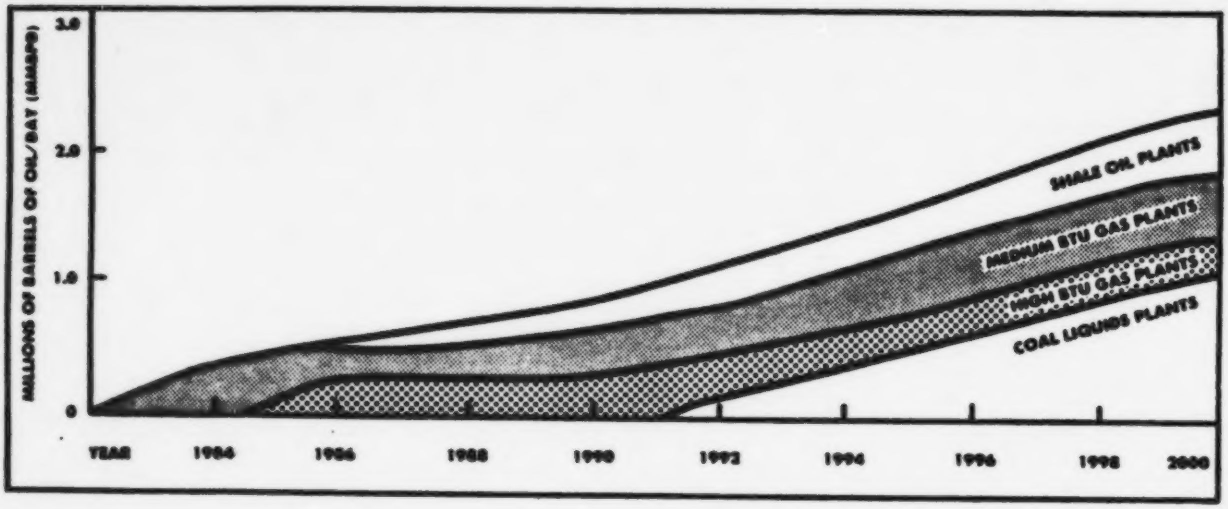


Figure 3. Synfuels Industry Buildup for the Nominal Production Scenario

For shale oil, a nominal production rate of 0.4 MMBPD should be achieved by the year 2000. The buildup rate is estimated to lag about 4 years behind that of Scenario I and is based on the following observations:

- Some technologies are still considered developmental, such as the modified in situ process.
- Land problems, including availability of off-tract disposal sites, may take longer to resolve.

Under this scenario, no large-scale commercial coal liquefaction plants are projected to be on line until 1992 with a growth rate beyond yielding 1 MMBPD by the year 2000. It is believed that Federal incentives will be applied to support construction of one each of the indirect liquefaction plants and a direct liquefaction plant only after sufficient assessment has been made of the operations of the EDS and H-Coal pilot plants and the SRC II demonstration plant. Rather than commit sizable resources to the commercialization of indirect liquefaction, a decision probably will be delayed resulting in no operating commercial liquefaction plants before 1992 under this scenario. During the 1980s it is believed that improvements will be made in both the operating indirect liquefaction plants and the designs of the direct liquefaction processes. These "advanced" technologies with product slates yielding primarily transportation fuels, will be sufficiently attractive to encourage development of 1 MMBPD of coal-derived liquid production by the year 2000.

Currently there is a great deal of interest in SNG technology. Several gas utility and pipeline companies have expressed plans to construct high-Btu plants. With incentives, several of these plants will be constructed and in operation by 1985. However, as a result of the projected improved outlook for gas supplies, including potential from unconventional sources, the availability of "imported" conventional natural gas (Alaskan, Canadian and Mexican) and the current unfavorable rate-structure pricing policy, the complete commercialization of HBG will be hampered. Its production rate is not likely to expand beyond the 0.25 MMBPD-level attained around 1992 under this scenario.

The buildup of medium-Btu gas plants will also be impeded by the availability of natural gas; however, for certain industrial applications requiring large volumes of uninterrupted supplies (e.g., chemical feedstocks, cogeneration) low-/medium-Btu plants will remain attractive. It is estimated that production of low-/medium-Btu gas will reach a level of 0.45 MMBPD by 1992.

ACCELERATED PRODUCTION - SCENARIO III

The accelerated production scenario is based on the assumption that Federal incentives are sufficient to synfuels production to meet the national goals in 1992, that operation of synfuels plants up to 1992 is successful to the extent confidence in processes is gained, and all resource requirements are satisfied. Licensing and permitting procedures must also be streamlined. It is assumed that demand for coal-derived synfuels remains at a level such that new plant capacity continues to be added to the year 2000 at about the same rate as the buildup to 1992. For shale oil, the production of 0.9 MMBPD by the year 2000 is based on a survey and analysis of the desired goals of each industrial developer. As indicated in Figure 4, a total synfuels production rate of 5 MMBPD may be reached by the year 2000. This includes 2.6 MMBPD of coal liquids, 1.5 MMBPD of gas and 0.9 MMBPD of shale oil.

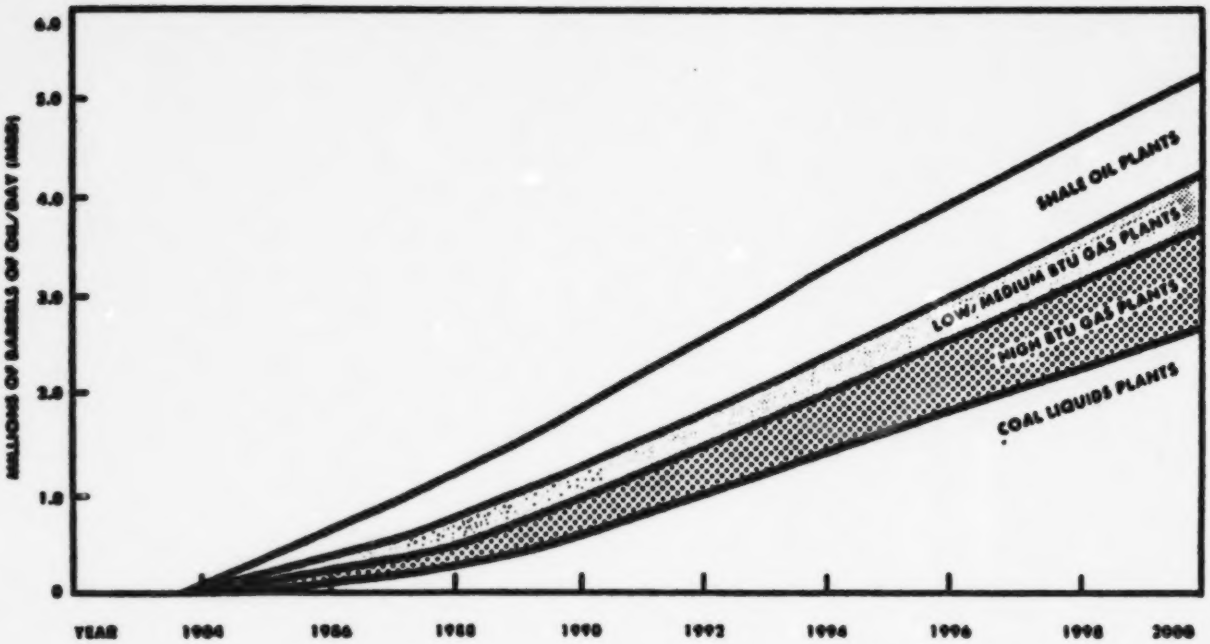


Figure 4. Synfuels Industry Buildup for the Accelerated Production Scenario

However, in view of the limitations facing the synfuel industry, some of which were discussed earlier, the accelerated production scenario is highly unlikely. The synfuels industry buildup rate (Figure 4) for this scenario can be considered an upper bound to synfuels utilization over the next 20 years.

The three scenarios describing possible synfuel industry buildup profiles provide a basis for projecting the market penetration of synfuel products in the near future. As these products enter the market, potential environmental impacts related to synfuels utilization must be considered.

THERE IS A LARGE POTENTIAL MARKET FOR SYNFUEL PRODUCTS AND BY-PRODUCTS

The major synfuel products could be broadly classified into five groups:

- Gaseous Products
    - High-Btu gas
    - Medium-Btu gas
    - Low-Btu gas
    - Liquified Petroleum Gas (LPG)
- Light Distillates
    - Gasoline
    - Naphtha
- Middle Distillates
    - Jet fuel
    - Kerosenes
    - Diesel oil
- Residue
    - Heavy fuel oil
    - Lubricants
- Petrochemicals.

GASEOUS PRODUCTS

The high- and medium-Btu gases are suitable for essentially all industrial fuel applications that can be serviced by coal, oil or natural gas. In some cases equipment modifications or special controls will have to be implemented to retrofit existing plants for medium-Btu gas, whereas this problem may not exist for high-Btu gas installation. However, there should be no difficulty in employing either high- or medium-Btu gas in new industrial installations. These products will be utilized by major energy consuming industries such as food, textile, pulp and paper, chemicals, and steel. It appears that only chemical, petroleum, and steel industries will require sufficient fuel gas at a single location to economically justify the dedication of a single gasification plant. Other industrial plants will have to share the output distributed by pipeline from a central gasifier, or tap into the existing natural gas pipeline system for their need. Preliminary economic studies indicate that it is not economical to transport medium Btu gas through pipelines for more than 200 miles. Medium-Btu gas can also be utilized by the petrochemical industries as chemical feedstock for the production of ammonia, methanol, and formaldehyde. Currently most of this requirement is met by reforming natural gas. The use of medium-Btu gasification appears especially attractive when integrated with new combined plants for utility applications.

The major characteristics of low-Btu gas are its high nitrogen content, low carbonmonoxide and hydrogen content, and resulting heating value typically below 150 Btu/SCF. Its flame temperature is also about 13 percent lower than that of natural gas. Because of these characteristics low-Btu gas is limited to on-site use, industrial processes requiring temperature below 2800^{o}-3000^{o}F, and is generally unsuitable for use as a chemical feedstock. Further, because of its low energy density it requires significant equipment modifications for retrofit applications. Today there are operating and planned low-Btu gasifiers in the U.S. for:

- Kiln firing of bricks
- Iron ore pelletizing
- Chemical furnace
- Small boilers

Liquified petroleum gas (LPG) has applications for industrial, domestic, and transportation uses. In domestic applications LPG is used mainly as a fuel for cooking and for water and space heating. In industry, LPG finds a large number of diverse outlets. Apart from use as a fuel in processes which require careful temperature control (glass and ceramics, electronics) or clean combustion gases (drying of milk, coffee, etc.), LPG is also used in the metallurgical industry to produce protective atmospheres for metal cutting and other uses. The chemical industry, particularly on the U.S. Gulf Coast, uses petroleum gases for cracking to ethylene and propylene as well as for the manufacture of synthesis gas. Small portions of LPG are also used to fuel automotive vehicles. Another use of LPG is to enrich lean gas made from other raw materials to establish proper heating value levels. On a volume basis, production of LPG in the U.S. exceeds that of kerosene and approaches that of diesel fuel. About 40 percent of LPG production is used by the chemical industry, another 40 percent is for domestic use, 10 percent for automotive use, and the remaining distributed among other industrial and agricultural fuel uses. Currently LPG is supplied primarily from refineries handling petroleum crudes. With the anticipated shortfall in the supply of these crudes, the resulting shortage of LPG will be met to some extent by LPG from synfuel plants.

LIGHT DISTILLATES

Gasoline, which is a major light distillate, is generally defined as a fuel designed for use in reciprocating, spark ignition internal-combustion engines. Other uses for gasoline are of small volume. Primarily it is used as fuel for automotive ground vehicles of all types, reciprocating aircraft engines, marine engines, tractors and lawn mowers. Other small-scale uses include fuel in appliances such as field stoves, heating and lighting units, and blow torches. By far the primary use of gasoline produced from coal will be for transportation applications. Currently we consume nearly 6.8 MMBPD of petroleum-derived gasoline and this corresponds to about 40 percent of the total petroleum consumption.

Naphthas have a wide variety of properties and serve many industrial and domestic uses. Their primary market is the petrochemical industry where they can be used for the manufacture of solvents, varnish, turpentines, rust-proofing compounds, pharmaceuticals, pesticides, herbicides, and fungicides. However, preliminary analysis indicates that there will be a relatively small amount of coal-derived naphthas entering the market.

MIDDLE DISTILLATES

The market for middle distillates, which essentially are jet fuel, kerosene, diesel oil and light fuel oil, are jet aircraft, gas turbines, and diesel engines used for transportation and stationary applications, and residential and commercial heating.

RESIDUES

The market for residues, consisting mainly of fuel oil, is primarily for industrial, utility and marine fuel use. Other applications for residues include preparation of industrial and automotive lubricants, metallurgical oils, roof coatings, and wood preservative oils. Coke is another likely useful product from residue.

PETROCHEMICALS

Many synfuel products, in addition to their primary use as fuel, are likely to be used by the petrochemical industry for the production of several other by-products. Currently over 3000 petrochemical by-products are derived from petroleum and natural gas sources. These include items like synthetic rubbers, plastics, synthetic fibers, detergents, solvents, sulfur, ammonia and ammonia fertilizers and carbon black.

Petrochemicals from synfuels will generally fall under three broad groups based on their chemical composition and structure: aliphatic, aromatic, and inorganic. An aliphatic petrochemical is an organic compound which has an open chain of carbon atoms. Important petrochemicals in this group include acetic acid, acetic anhydride, acetone, ethyl alcohol, and methyl alcohol. Most aliphatic petrochemicals are currently made from methane, ethane, propane or butane. Aliphatics currently represent over 60 percent of all petrochemicals and are the most important group economically.

An aromatic petrochemical is also an organic compound but one that contains or is derived from a basic benzene ring. Important in this group are benzene, toluene, and xylene, commonly known as the B-T-X group. Benzene is widely used in reactions with other petrochemicals. With ethylene it gives ethyl benzene which is converted to styrene, an important synthetic-rubber component. As a raw material it can be used to make phenol. Another use is in the manufacture of adipic acid for nylon. Toluene is largely used as a solvent in the manufacture of trinitrotoluene for explosives. Xylene is used as a source of material for polyester fibers, isophthalic acid, among other petrochemicals.

An inorganic petrochemical is one which does not contain carbon atoms. Typical here are sulfur, ammonia and its derivatives such as nitric acid, ammonium nitrate, ammonium sulfate.

The different end-use applications of major synfuels products are summarized in Table 7. We see from this discussion that coal-derived synfuel products are likely to be used not only as a fuel, but also in the manufacture of a number of other by-products which will be used in multitudes of other applications.

Table 7. Major End-Use Applications of Synfuel Products

Major Synfuel Products	Likely Major End Use Applications
High and medium Btu gas	Food, textile, pulp and paper, chemicals, iron and steel industries; residential/ commercial heating
Low Btu gas	Small boilers, kilns, pelletizing
LPG	Glass, electronics, chemical industries; domestic cooking and heating; automotive
Gasoline	Transportation
Naphtha	Petrochemical industry; solvents; varnish; turpentines
Middle distillates (kerosene, diesel, light fuel oil)	Transportation, gas turbines, residential and commercial heating
Residues	Industrial, utility and marine fuel; matallurgical oils; roof coatings; wood preservatives, lubricants

ANTICIPATED SYNFUELS MARKET PENETRATION IN THE VARIOUS SECTORS OF THE U.S. ECONOMY WILL EXPAND OVER TIME

As an indication of the time frame over which the EPA must consider issues regarding the use of various synfuel products, market development and penetration of these products must be anticipated. For example, the synfuels market may develop as illustrated in Figures 5, 6 and 7, over 1985-1987, 1988-1990 and 1991-2000 time frames.

SYNFUEL PRODUCT UTILIZATION EMPHASIS, 1985-1987

Oil shale-derived synfuels will be introduced into the petroleum product markets about 1985, and based on Scenario I as much as 0.2 MMBPD of shale oil can enter the market by I987. The first stage of synfuels market infrastructure development will be oriented towards transportation fuels (reference Figure 5) because oil shale that is hydrotreated can be refined in existing refineries to such products as gasoline, jet fuel, diesel and marine fuels. The bulk of this supply will be in the form of middle distillates comprised of jet fuel and diesel oil. The demand for transportation during the late 1980s is expected to be around 10 MMBPD. Of this, about 5 percent is likely to be consumed by the military sector. It is conceivable, therefore, that the bulk of the shale oil products could be utilized by the military, possibly with a Government synfuel purchase guarantee program.

It is anticipated that the oil shale industry will continue to grow producing as much as 0.45 MMBPD by year 2000 as per Scenario I and II and as much as 0.9 MMBPD as per Scenario III. The Bulk of this production is anticipated for the transportation sector.

SYNFUEL PRODUCT UTILIZATION ADDITIONS, 1988-1990

Subsequent buildup of the synfuels industry during the 1988-1990 time period (reference Figure 6) is expected to come from commercial-size, high-Btu gasifiers. As per Scenario 1, the output from these high-Btu gasifiers may be as high as 0.4 MMBPD of oil equivalent by 1990; however, the conservative estimate based on Scenario II is that only around 0.17 MMBPD of oil equivalent is likely to be produced by that time. The high-Btu gasification will serve some of the energy needs of both the industrial and residential/commercial sectors as direct gas sales or through electric

SYNFUEL UTILIZATION DURING 1985-1987

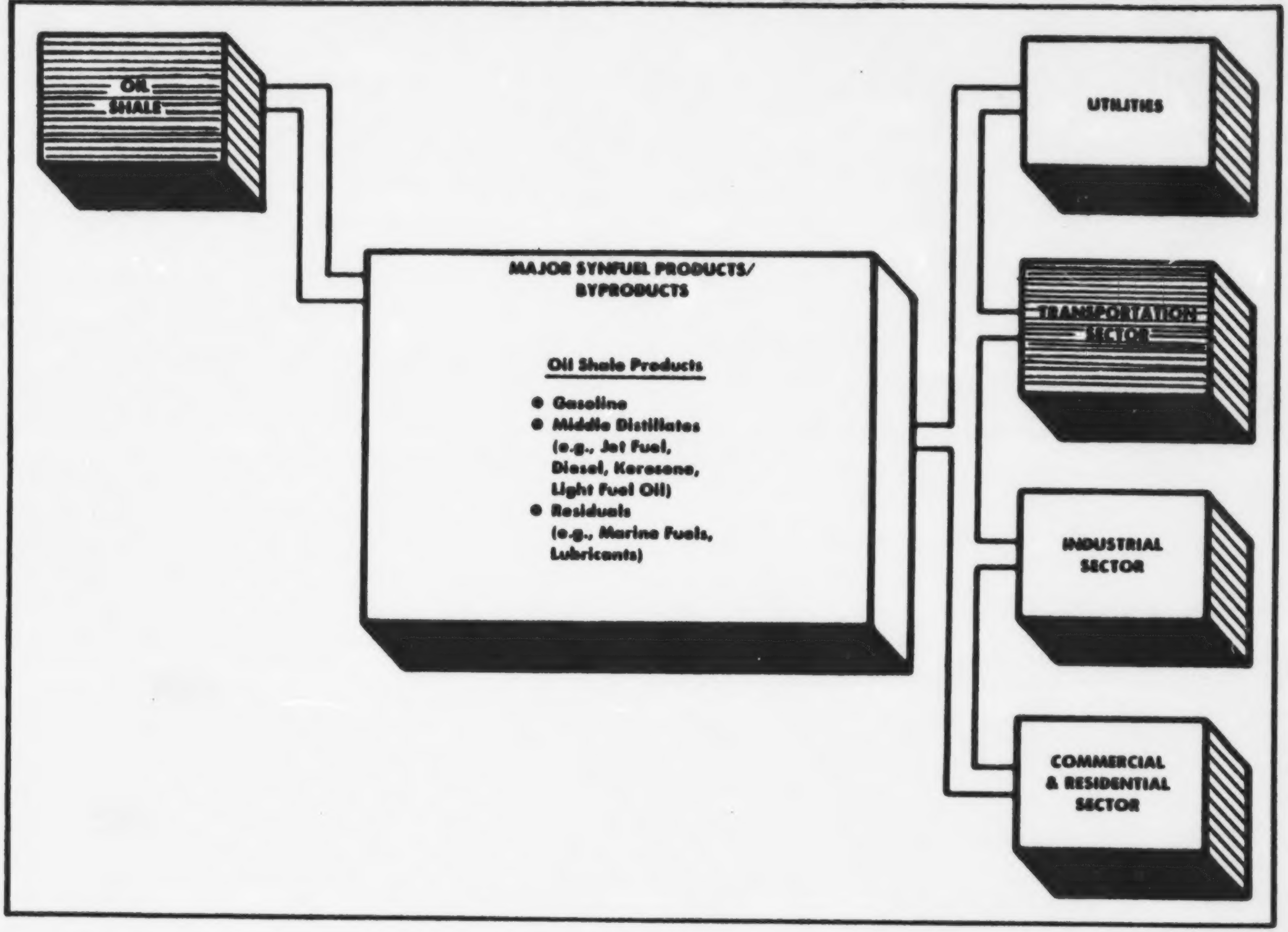

OIL SHALE
MAJOR SYNFUEL PRODUCTS/ BYPRODUCTS
Oil Shale Products
● Gasoline
● Middle Distillates (e.g., Jet Fuel, Diesel, Kerosene, Light Fuel Oil)
● Residuals (e.g., Marine Fuels, Lubricants)
UTILITIES
TRANSPORTATION SECTOR
INDUSTRIAL SECTOR
COMMERCIAL & RESIDENTIAL SECTOR

Figure 5

SYNFUEL UTILIZATION DURING 1985-1990

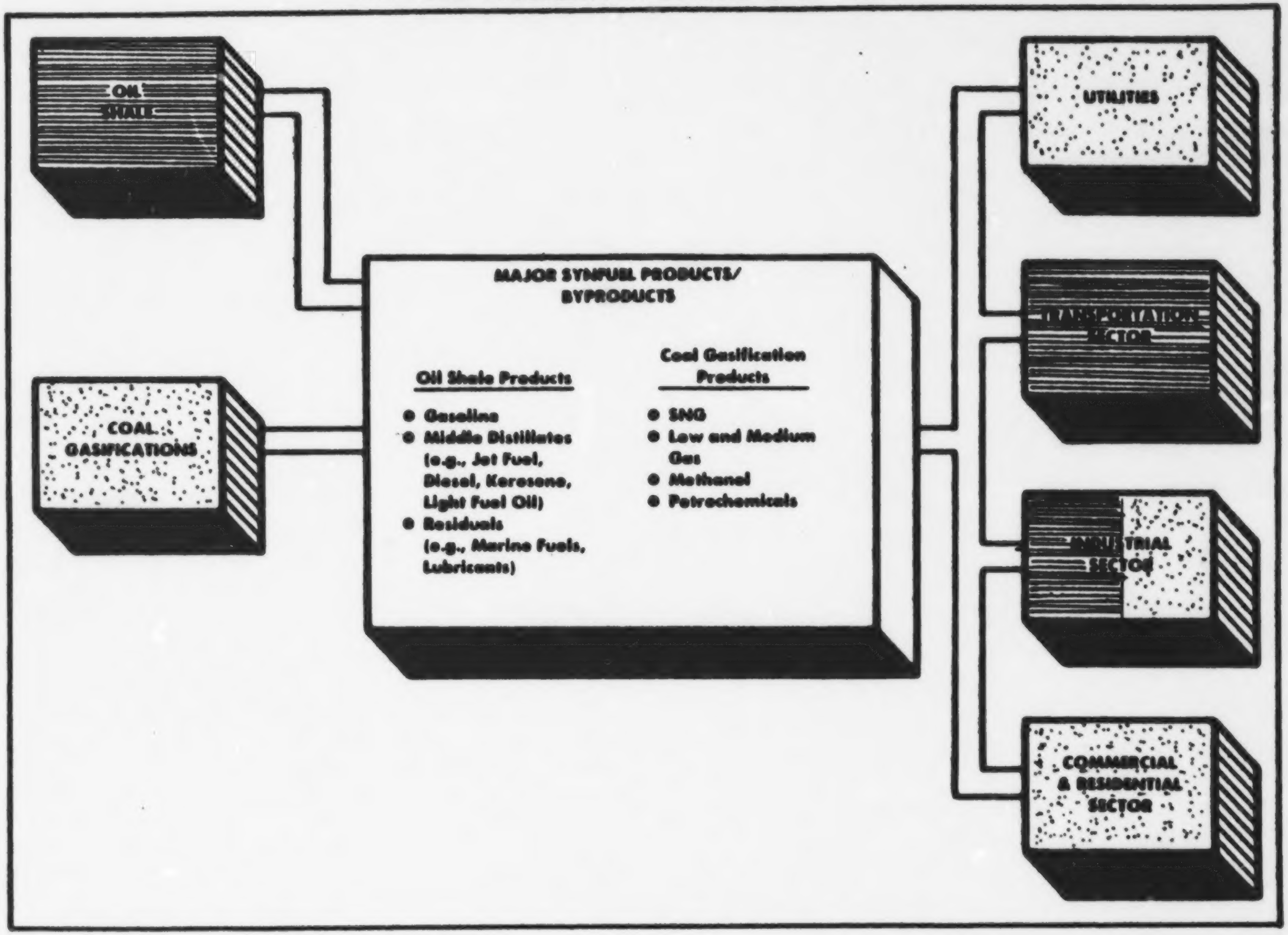

OIL SHALE
COAL GASIFICATIONS
MAJOR SYNFUEL PRODUCTS/ BYPRODUCTS
Oil Shale Products
● Gasoline
● Middle Distillates (e.g., Jet Fuel, Diesel, Kerosene, Light Fuel Oil)
● Residuals (e.g., Marine Fuels, Lubricants)
Coal Gasification Products
● SNG
● Low and Medium Gas
● Methanol
● Petrochemicals
UTILITIES
TRANSPORTATION SECTOR
INDUSTRIAL SECTOR
COMMERCIAL & RESIDENTIAL SECTOR

Figure 6

SYNFUEL UTILIZATION DURING 1985-2000

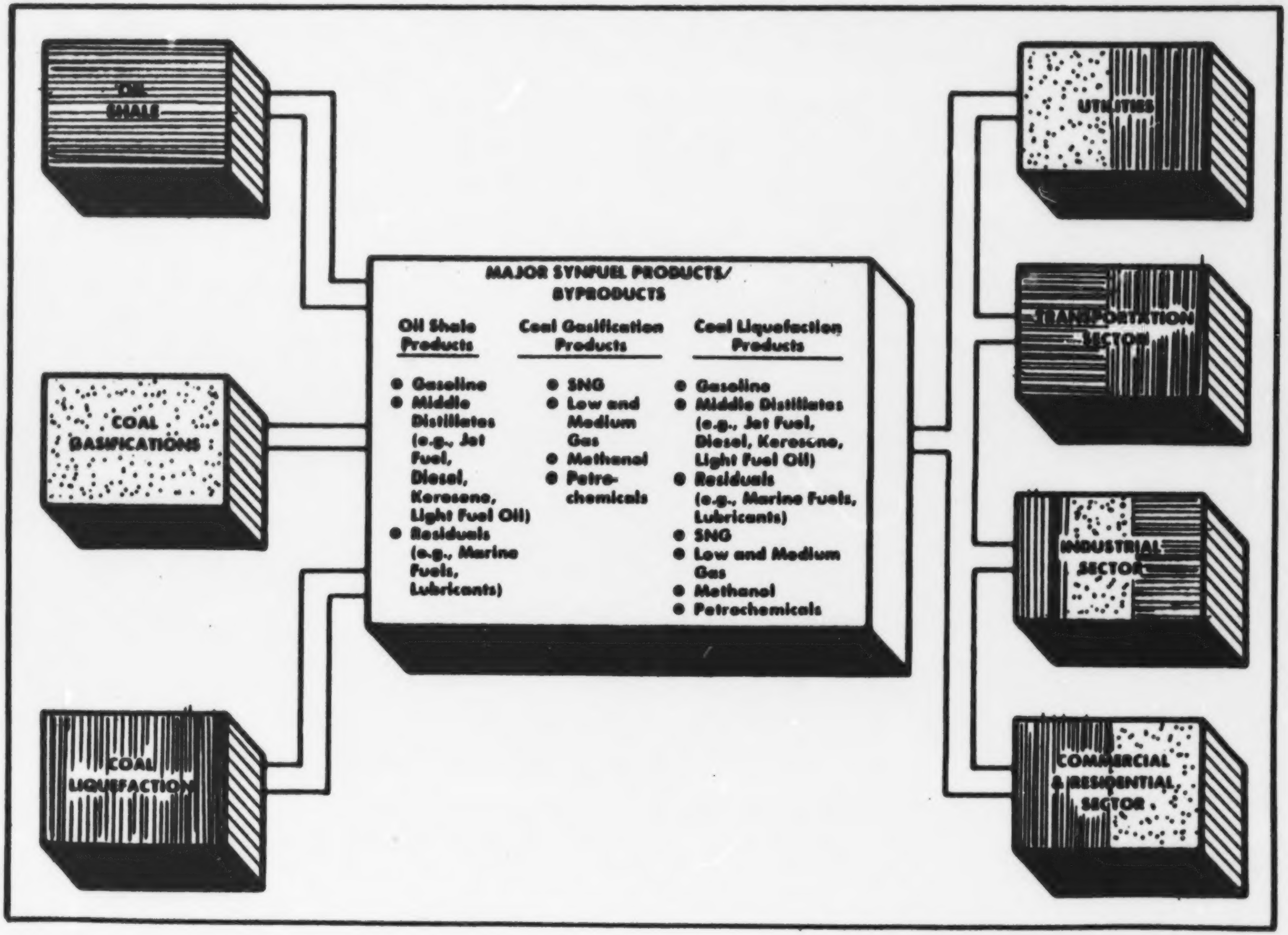

OIL SHALE
COAL GASIFICATIONS
COAL LIQUEFACTION
MAJOR SYNFUEL PRODUCTS/ BYPRODUCTS
Oil Shale Products
● Gasoline
● Middle Distillates (e.g., Jet Fuel, Diesel, Kerosene, Light Fuel Oil)
● Residuals (e.g., Marine Fuels, Lubricants)
Coal Gasification Products
● SNG
● Low and Medium Gas
● Methanol
● Petrochemicals
Coal Liquefaction Products
● Gasoline
● Middle Distillates (e.g., Jet Fuel, Diesel, Kerosene, Light Fuel Oil)
● Residuals (e.g., Marine Fuels, Lubricants)
● SNG
● Low and Medium Gas
● Methanol
● Petrochemicals
UTILITIES
TRANSPORTATION SECTOR
INDUSTRIAL SECTOR
COMMERCIAL & RESIDENTIAL SECTOR

Figure 7

power generation by utilities. Some of the major industrial users of high-Btu gas are likely to be textile, food, steel, and chemical industries. Initially, following the current use pattern, it will be used not only as an industrial fuel but also as a chemical feedstock. It is expected that the existing natural gas pipeline network, with the exception of a few connecting pipelines, will be utilized for the distribution of high-Btu gas and, therefore, introduction of high-Btu gas is not likely to cause major problems concerning distribution for end-use applications. During this time period it is also likely that low- and medium-Btu gasification plants will be used by industries in a captive mode to supply some of their fuel and chemical feedstock needs. This may amount to as much as 0.3 to 0.4 MMBPD of oil equivalent based on the first two scenarios. The medium-Btu gas could be used as a synthesis gas for the production of different chemical products such as ammonia which in turn could be used for the manufacture of such products as fertilizers, fiber and plastic intermediates, and explosives. Currently the petrochemical industry derives its synthesis gas by reforming natural gas or naphtha. During this time period, it is likely that one to three small plants possibly producing methanol from medium-Btu gas may come on line. These are likely to be owned by industries primarily to supply internal needs. This could be for the production of formaldehyde, a product with a number of end-use applications. It is unlikely that products from these plants will be entering the open market directly, on a large scale, for public consumption. During this time period the use of low-Btu gas will be limited to an industrial fuel in such applications as kilns, chemical furnances and small boilers. However, the use of low-Btu gasification by utilities in one or two demonstration units for combined-cycle applications cannot be ruled out.

During this time frame the shale oil output will continue to grow reaching as much as 0.4 MMBPD in accordance with the National Goal Scenario. As a result it is anticipated that increasing amounts of shale oil products will be entering the transportation sector, with limited entry into the industrial sector for use as fuel.

SYNFUEL PRODUCT UTILIZATION ADDITIONS, 1991-2000

During the 1991-2000 time frame (reference Figure 7), central coal liquefaction plants will introduce into the market a spectrum of products and by-products that will be consumed by the transportation, industrial, and residential/commercial sectors. Based on the nominal and accelerated scenarios, by the year 2000 1.5 to 2.5 MMBPD of coal liquid products will be entering the market. Under these conditions, a significant segment of the transportation fleet could be running on synthetic fuel. Coal-derived liquids will be utilized not only by industry as a fuel source and chemical feedstock, but also by the residential and commercial sectors for space heating, hot water supply and other domestic uses. Furthermore, many of the oil-fired utility plants given exemption from converting to coal in the interim will be burning coal-derived fuel oil. SRC II plants will be the likely candidate which will be supplying the bulk of this fuel. It is also expected that methanol from indirect coal liquefaction could be entering the market for use as turbine fuel for the production of electricity, during this time period. In addition, SNG produced from the liquefaction processes will be also entering the market, supplementing the output from high-Btu gasification plants. The SNG output from liquefaction plants could be as high as 20 percent of the total useful output from these plants in terms of heating value. LPG and naphtha produced from direct and indirect coal liquefaction processes and oil shale are likely to be used primarily by the petrochemical industries. For example, LPG may be used by the petrochemical industry as a raw material for the production of alcohols, organic acids, detergents, plastics, and synthetic rubber components. Naphthas may be utilized for the manufacture of such items as solvents, adhesives, pesticides, and chemical intermediates. Currently the petrochemical industry uses about 11 percent of our crude oil supply for the production of various petrochemicals. During the 1990-2000 time frame, it is possible that the same percentage of available synfuels will be utilized by the petrochemical industry for the production of hundreds of petrochemical products. A major use of residuals from coal liquefaction processes and oil shale is likely to be the manufacture of different types of lubricants. These could be for such applications as lubrication of engines and general machinery, steam turbine bearings and reduction gears, compressors, insulating oils, metal working and cutting oils.

So we see in the above discussion that the synfuels products and by-products are likely to enter all the end-use sectors, in course of time. The potential for exposure and for environmental impacts must be carefully considered. Early planning by the EPA will require that synfuel products/by-products be assessed with regard to their environmental acceptability.

POTENTIAL ENVIRONMENTAL EXPOSURES DUE TO SYNFUELS UTILIZATION

A major concern of the emerging synfuels industry is the potential environmental, health and safety impacts associated with the use of synfuels. The potential exposure of the public to synfuels will depend on the rate of development of the synfuels industry's specific end-use markets. Since the market may cover a wide range of products and end uses, a significant portion of the population may be exposed. The products will enter the markets in varying quantities over the coming years. To illustrate the important environmental concerns, synfuels product production rates based on the National Goals Scenario (Scenario I) are considered and three time periods are examined for potential environmental exposure, 1985-1987, 1988-1990, and 1991-2000.

POTENTIAL EXPOSURES: 1985-1987

During this period, synfuels entering the market will be mostly limited to shale oil products. Approximately 0.2 MMBPD of products by 1987 is projected by Scenario I. Crude shale oil will most likely be transported to refineries in either the Gulf Coast or Midwest and is expected to be distributed by existing pipelines. Product quantities will be limited. The hazards of transporting and storing crude shale oil and shale oil products are expected to be minimal. Shale oil products will be used primarily as transportation fuels such as gasoline, diesel oil, and jet fuel and will be distributed by railroads, tankers, trucks and barges. During this period the quantities handled are estimated to amount to 0.04 MMBPD of gasoline and a combined total of 0.16 MMBPD for the middle distillates. The major exposure to these products occur at storage terminal unloading operations and service station storage tank loading operations, both of which have high spill potential. The end user (a passenger car, truck, or other vehicle) also poses a potential spill problem due to the rapid expansion of self service stations. Combustion of the fuels may expose a large segment of the population since most automobile traffic is generated in central business districts and their suburbs. By-products from shale oil refining such as lubricating oils and greases will be shipped from refinery bulk packing plants in secure containers, minimizing the likelihood of exposure.

Products from shale oil production could reach approximately 0.3 to 0.4 MMBPD during this period, as suggested by the accelerated rate scenario, with the potential exposure reaching twice the level suggested by the National Goal Scenario.

POTENTIAL EXPOSURE: 1988-1990

During this period, in addition to increased shale oil production, SNG low and medium Btu gas, and some indirect liquefaction products will also be entering the market, which increases the complexity of the synfuels distribution network and increases the potential for public exposure to the products. It is a time period by which the EPA must have identified potential problems and have developed a plan for meeting the synfuels challenge.

Shale oil production during this period is projected to be 0.3 to 0.4 MMBPD under the National Goal Scenario, but could range from 0.2 MMBPD (nominal production rate scenario) to 0.8 MMBPD (accelerated production rate scenario) in 1990. The exposure potential to the products will increase proportionally during this time period compared to the previous period.

The SNG entering the market is projected to amount to an oil equivalent of 0.4 MMBPD by 1990, and will be transported by existing pipeline to the various markets. Although pipelines transporting SNG or crude shale oil present a low accident potential, pipelines either transect or terminate in densely populated areas, providing some degree of exposure potential to these products. First generation coal gasification technology (Lurgi) buildup will occur near western U.S. coal deposits, the Northern Great Plains/Rocky Mountains area. The SNG from this area will enter the northern tier pipeline network and will be distributed across the upper Midwest. Medium- and low-Btu gases will also be in the market during this period, although they will probably be used for internal plant needs. This will minimize the exposure potential since these gaseous products will not require any transportation.

Some synthetic gases have different compositions than natural gas, and may cause internal corrosion and stress-corrosion cracking in pipelines. Effects of impurities on the long-term degradation of some pipeline materials are unknown. Synthetic gaseous fuels also have different flammability and explosion limits that may require new techniques in the management of pipeline leaks. Gases with a high CO concentration are toxic and could present significant exposure problems.

In addition to their use in transportation and boiler applications, synfuels products will be used as feedstocks for industrial processes. These applications, although limited during this time period, present another avenue of exposure for which EPA must be prepared. The population exposed could include industrial plant personnel as well as the end users of the industrial products. During this period, medium-Btu gas could be used as a synthesis gas for the production of methanol and ammonia, each of which can be utilized as a finished product.

Although this period will be characterized by the emergence of many synfuels products, the main population exposure potential will occur from crude shale oil transport by pipelines, product storage and the combustion of these products.

A basic environmental concern with the transportation of liquid synfuels is the possibility of an accidental spill. A recent (1979) Department of Transportation analysis shows that of all the accidents resulting from pipelines carrying liquid petroleum products, the largest spillage occurs from LPG (58.6 percent) followed by crude oil (25.3 percent), with fuel oil (6.1 percent) and gasoline (4.5 percent) being the other major contributors.

As an example to illustrate the relative exposure of transporting petroleum products by pipeline in order to provide an awareness of the potential exposure in transporting shale oil, Table 8 presents a listing of oil pipeline accidents. Since existing pipelines will be used during this time period for transporting crude shale oil, these potential exposures and risks in each component of the carrier system must be considered by EPA.

Table 8. Number of Oil Pipeline Carrier System Accidents

YEAR	79	78	77	76	75	74	73	72	71
Line Pipe	207	194	177	169	185	203	215	238	264
Pumping Station	20	30	32	11	24	13	23	31	14
Delivery Point	6	4	4	4	5	5	5	3	2
Tank Farm	5	15	12	14	30	22	21	24	11
Other	11	13	12	14	10	13	9	10	19
Total Accidents	249	256	237	212	254	256	273	306	310

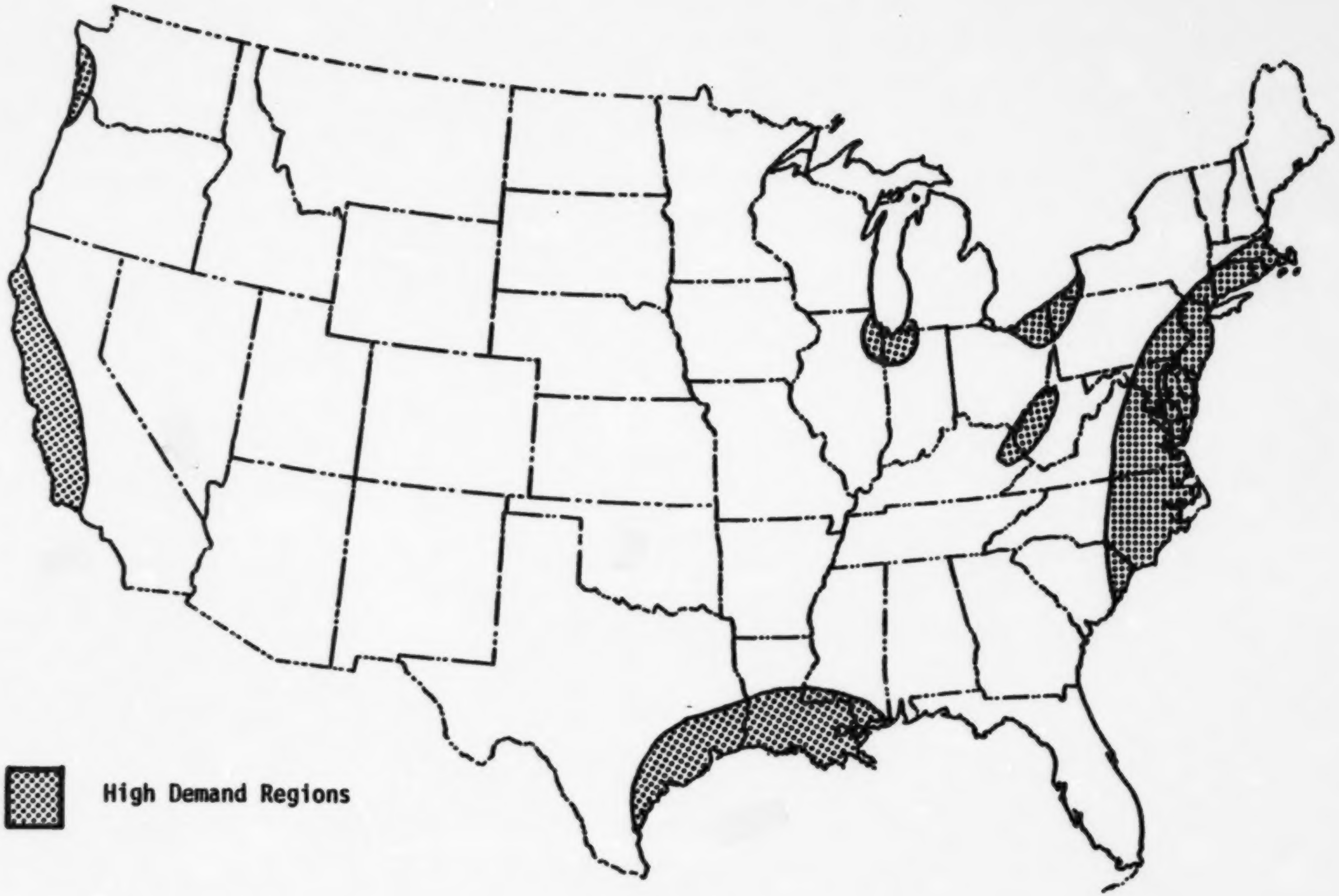
Source: Department of Transportation

POTENTIAL EXPOSURE: 1991-2000

This period is characterized by the large-scale entry into the market of direct and indirect liquefaction products and by-products for use primarily by the transportation, industrial and utility sectors. Based on the National Goal Scenario, 1.0 MMBPD of coal liquids will be in the market by 2000, but may range up to 2.5 MMBPD. Utility and industrial boiler fuels produced by coal liquefaction processes will be most in demand in the Gulf Coast, Northeast, and Southern California regions, as shown in Figure 8. These regions contain a significant portion of the U.S. population. The use of these fuels will also have some beneficial effect in areas that are sensitive to particulate and sulfur dioxide since these fuels have lower ash and sulfur contents. As more liquefaction capacity develops in the Appalachian and interior regions, liquid fuels will more readily be used in the industrial areas of Indiana, Illinois, Ohio, and the upper Northwest. Shale oil products during the period may reach a level of 0.4 MMBPD under the National Goal Scenario and could reach as high as 0.9 MMBPD under the accelerated rate scenario. High-Btu gas under these two scenarios is estimated at 0.5 MMBPD and 1.0 MMBPD respectively by 2000. As coal gasification technology develops, it is likely that a key area for gasification will eventually be Appalachia, with SNG entering the existing pipelines and being distributed along the east coast to both industrial and residential users.

This period is also characterized by increased use of coal liquid products for chemical feedstocks and in the housing and commercial sectors

Figure 8. Potential Regions for Synfuel Demand for Industrial Fuel Application


▨ High Demand Regions

for space heating and hot water supply. Naphthas produced by liquefaction processes are likely to be used by the petrochemical industries for manufacturing solvents, pesticides and chemical intermediates. Residues from coal liquefaction processes may be used to manufacture several types of lubricants with a wide variety of applications. This market penetration significantly increases exposure potential as there is virtually no segment of the population that would be excluded from the use of synfuel products and by-products.

In addition to synfuels utilization, EPA must also consider the transportation and handling aspects of the synfuels products and by-products. As the synfuels develop during this period, transportation modes other than pipelines will be utilized. Although there are associated risks, pipelines are considered to present less risk than other modes such as railroads, trucks, and tankers. As these modes are currently used for a wide variety of petrochemical products, it is expected that they will also be used as synfuels penetrate the market, thereby presenting another concern that EPA must address.

Table 10 presents an estimate of the range of synfuel products to be shipped by the various transportation modes beginning in the 1990s. Nearer to the year 2000, the relative amounts of products transported between the modes may vary. The majority of the synfuel products as well as crude shale oil will be transported by pipelines, which presents the least amount of exposure potential. On the other hand, railroads which have a high accident potential will transport the least amount of products. In order to supply the high demand regions (reference Figure 8) the transport distribution networks may develop as illustrated in Figure 9. The distribution system indicates that the crude shale oil, refined products, SNG, and coal liquids will each be transported across areas of high population density and industrial concentration, mostly in the eastern U.S. A market for 2.2 MMBPD of synfuels products and by-products by 1992 under the National Goals Scenario indicates the magnitude of the problem for which EPA must prepare.

The transportation modes that will be utilized by the synfuels industry and which pose a greater accident potential than pipeline transport are railroads, trucks and tankers. Railroads will be used

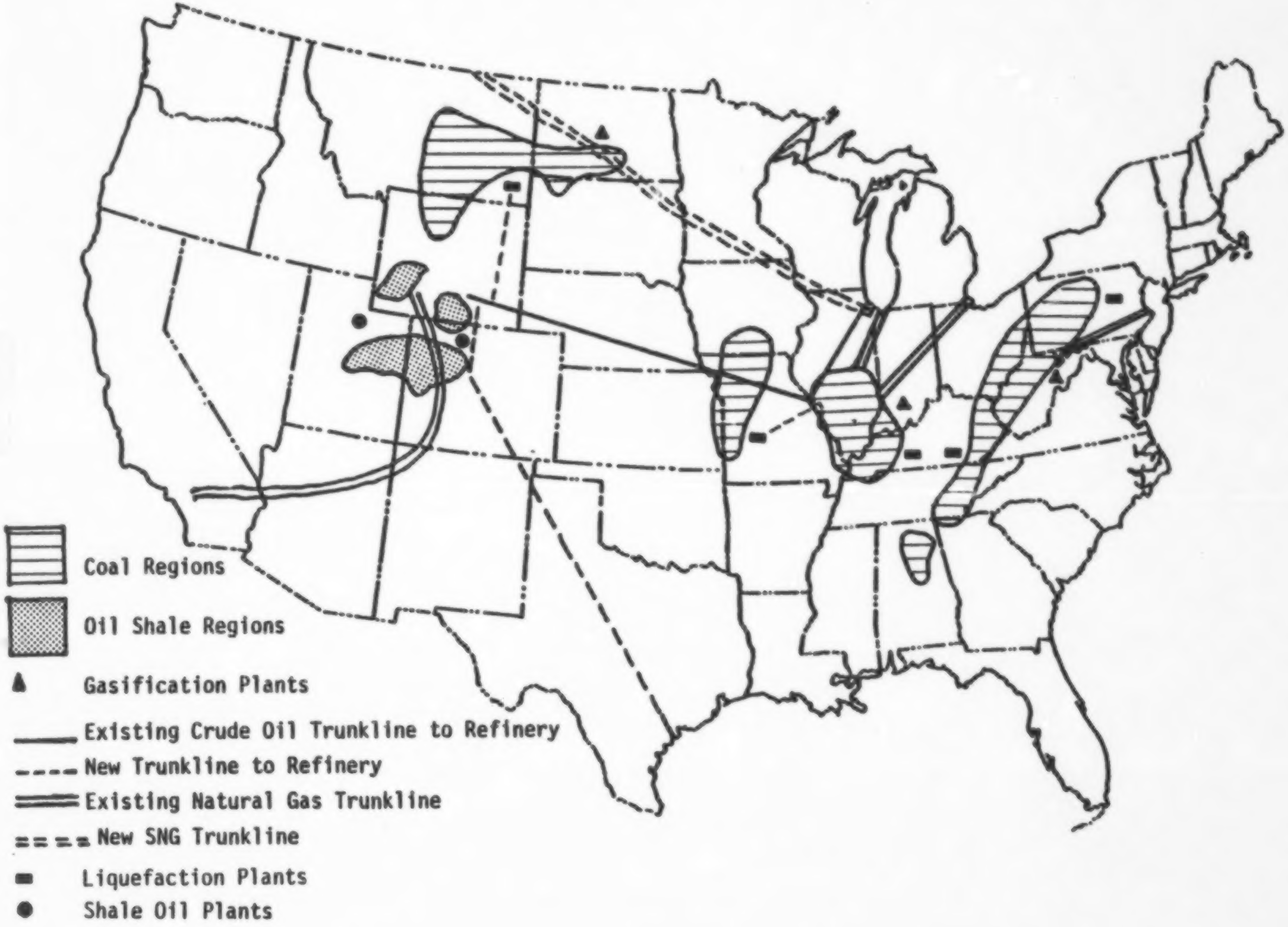
Table 10. Range of Synfuels Distributed by Mode of Transportation in the 1990's

SYNFUEL PRODUCT	PIPELINE	RAIL	TRUCK	TANKER OR BARGE
HI Btu GAS (MMSCFD)(2)	1900 - 4800	0	0	0
MEDIUM Btu GAS (MMSCFD)	8300 - 5600	0	0	0
LIQUEFACTION PRODUCTS (MMBPD)				
HEAVY FUEL OILS AND MIDDLE DISTILLATES	0.025 - 0.080	0	0.014 - 0.044	0.007 - 0.022
GASOLINE	0	0	0.072 - 0.520	0.018 - 0.130
NAPHTHA	0	0.042 - 0.067	0.005 - 0.008	0.005 - 0.008
LPG	0	0	0.0 - .018	0.0 - 0.005
CRUDE SHALE OIL (MMBPD)	0.389 - 0.750	0	0	0
REFINED·SHALE (MMBPD)				
GASOLINE	0.040 - 0.076	0	0	0.026 - 0.051
JET FUEL	0.047 - 0.090	0	0	0.031 - 0.061
DIESEL OIL	0.084 - 0.162	0	0.084 - 0.162	0.042 - 0.162
RESIDUAL OIL	0.025 - 0.047	0	0.004 - 0.007	0.007 - 0.014
ACCIDENT RISK	LOW	HIGH	HIGH	MODERATE

(1) MMSCFD = Million Standard Cubic Feet per Day

(2) MMBPD = Million Barrels per Day

Figure 9. Synfuel Resources and Distribution System in the 1990's


Coal Regions
Oil Shale Regions
Gasification Plants
Existing Crude Oil Trunkline to Refinery
New Trunkline to Refinery
Existing Natural Gas Trunkline
New SNG Trunkline
Liquefaction Plants
Shale Oil Plants

primarily for the transportation of naphthas which in 1992 are estimated to range from 0.04 to 0.07 MMBPD. This mode of transportation presents a high degree of accident risk due to the poor condition of the Nation's rail system. Derailments, grade crossing accidents, and collisions between trains pose potential risks to the transportation of any hazardous or toxic substances. Tank car accidents with hazardous materials are shown in Table 11, providing another example of potential risks associated with transporting synfuels products.

Table 11. Railroad Tank Car Accidents with Hazardous Materials

	1979	1978
Total Accidents	937	1014
Accidents Involving Atmospheric Release	165	228

Source: Federal Railway Administration

The use of tanker trucks will be extensive in transporting coal liquids and refined shale oil products. In 1992 under the National Goal Scenario, approximately 0.4 MMBPD of gasoline from coal liquefaction may be transported by truck, and up to 0.5 MMBPD under the accelerated rate scenario. Other products using this mode are middle distillates and naphthas. Potential exposure to the general population is high with tanker trucks since much of these products will be delivered to urban areas where trucks will face the normal amount of traffic accidents in congested areas. In addition, exposures to the products will occur in loading and unloading of trucks at storage terminals and service stations. Due to vapor recovery requirements mandated by state implementation plans, evaporative emissions of volatile compounds are gradually being controlled, but pollution control systems must be improved to further reduce emissions. Accidents or defective emission control systems provide the chief potential for release of synfuels products by truck transport.

Tankers and barges will also be used for the transportation of the refined shale oil and coal liquids products and could be used extensively if the markets are accessible to the gulf coast. Under the National Goal

Scenario, 0.1 MMBPD each of gasoline and diesel oil may be transported by these modes in 1992. Other products to a lesser extent are naphtha, LPG, jet fuel, and residual oil. A significant amount of petrochemical products currently move along the Mississippi River to northern markets. The major emission source for this operation involves loading and unloading; however, the accident rate is less than that of surface transportation mode. As with truck loading, increased emission controls are being initiated for ship and barge loading which will significantly decrease evaporative emissions by the time the synfuels industry is developed. Improvements are also being made to reduce spills of petrochemical products into waterways. Reduction of accidental spills and prevention of intentional releases are currently under regulation by the Coast Guard and EPA.

In addition to transportation and handling, the storage of synfuel products and by-products may pose potential environmental problems. These problems may occur primarily with refined shale oil and coal liquids. As with other petroleum products they will be stored at bulk storage terminals until used. By 1992, a total of 1.4 MMBPD of synthetic liquids will be produced under the National Goal Scenario, and ranging up to 1.7 MMBPD under the accelerated rate scenario. Exposures to these products at the terminals may occur during the loading and unloading operations, as well as breathing losses from the tanks during product storage. The potential for exposure depends upon the volatility of the products and the frequency of loading operations. Since storage facilities are located at refineries, utility and industrial plants, airports and numerous other facilities, exposure potential is significant. Concern over the uncertainties of the constituents of synfuels may lead to storage procedures for these products that are more rigid, and new storage vessels or containers for liquids may be required under stringent specifications. Some emissions may also occur from low-level leakage.

As with other major control requirements for loading and unloading petroleum products, vapor recovery techniques for bulk storage facilities are being improved, primarily by the use of floating roof tanks. Synfuels such as SRC II liquids have vapor pressures similar to No. 6 fuel oil which has very low evaporative emissions and working losses compared to gasoline. Fugitive emissions of synfuels will always be present as they are with other petroleum products. However, there will be new control systems developed and emissions will be reduced over the next several years through improvements in emissions control procedures in transportation, handling and storage operations. Only after thorough toxicity testing of synfuel products and by-products can an assessment be made of whether synfuels transportation, handling and storage will pose environmental, health, and safety problems greater than those experienced in the petroleum refining and chemical manufacturing industries.

ENVIRONMENTAL CONTROL TECHNOLOGY NEEDED FOR SYNFUELS UTILIZATION

The utilization of synfuels products and by-products will require improvements in existing environmental control technology and the development of new technologies. In order to assess the control technology requirements, it is necessary to first understand the hazards associated with synfuel utilization. This may be accomplished by determining the constituents of synfuels products and by-products, their transformation upon use, and ultimate fate in the environment. These data in turn must be tied closely to the product buildup rate described in each of the scenarios since these impact the types of products produced and their rate of penetration into the market. Once these factors are understood, then control technology options may be evaluated. This cycle must be completed within the next 10 years in order for EPA to meet the synfuels challenge.

EXISTING DATA REGARDING HAZARDS OF SYNFUEL PRODUCTS IS SPARSE

At the current time there is a lack of sufficient data available to properly assess the potential risks associated with the utilization of synfuel products and by-products. The development of these data will require significant efforts on the part of the government, industry and the academic community to generate sound, reliable information to assure minimum risks to the health and welfare of the nation as synfuels are introduced into the market. This synfuels data base must contain not only accurate and representative information about the physical properties, chemical composition and biological activities of synfuels, but must also contain equally comprehensive data on the end uses of the products and by-products.

The DOE and EPA are presently conducting significant research efforts on synfuels product characterization. The results of some of the shale oil and coal liquid products are becoming available. An example of the preliminary analysis of these two products compared with petroleum crude is presented in Table 12. There are some similarities in the diaromatic content between shale oil and petroleum crude, with coal liquids having the highest content. This factor may be significant if a spill of these products occurred, as impacts on water pollution would be less than from coal liquids. A comparison between coal and petroleum derived gasolines is

Table 12. Diaromatic Content of Synthetic Crudes and Crude Oils

Constituent	Concentration[1], mg/g Typical Shale Oil	Coal Syncrude	Petroleum Crude
Naphthalene	1.39	1.68	0.87
2-Methylnaphthalene	0.91	3.47	1.04
1-Methylnaphthalene	0.68	1.11	0.75
Biphenyl	0.06	0.44	T
2, 6-Dimethylnaphthalene	0.10	0.81	0.08
1, 3/1, 6-Dimethylnaphthalene	1.63	3.01	1.48
2, 3-Dimethylnaphthalene	0.28	1.53	0.51
1, 5-Dimethylnaphthalene	0.03	0.67	0.08
1, 2-Dimethylnaphthalene	0.19	0.23	0.31
Acenaphthalene	0.26	2.19	0.30
Acenaphthene	T	0.30	ND
TOTAL	5.23	15.4	5.42

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[1] T = trace, ND = not detected

Source: Oak Ridge National Laboratory

presented in Table 13, indicating significant variations in aromatics and unidentified compounds. Due to the high aromatic content of the coal-derived gasoline, potential adverse health effects may occur from widespread use of this fuel in automotive applications. Some of the synfuels products and by-products may be classified as toxic chemicals under the Toxic Substances Control Act (TSCA).

Preliminary health effects studies have indicated that coal liquids have industrial toxicity ratings similar to those of benzoic acid, phosphoric acid, sodium tartrate, and polychlorinated biphenyls (PCB). Coal liquids have also been found to be less toxic than pesticides such as dieldrin and chlordane, and more toxic than crude petroleum and shale oil. Historical epidemiological and animal studies have established that coal tars and pitches from coal coking, gasification, and combustion possess a carcinogenic nature. Although these studies are not all directly comparable, it would appear that some high-boiling point products from direct liquefaction processes or from coal pyrolytic processes may possess a high degree of carcinogenicity.

It is apparent that although work has started in the right direction to assess synfuels hazards, much work still needs to be conducted. As the physical, chemical and biological results are analyzed, and potential risks evaluated, decisions can start to be made as to the various pollution control technologies that can be most effectively applied in the utilization of synfuels.

Table 13. Major Chemical Component Classes of Petroleum and Coal-Derived Gasoline

CHEMICAL GROUP	GASOLINE	
	Petroleum-Derived[1]	Coal-Derived[2]
Total Saturates	56.38 - 68.68	20.1 - 68.5
Total Alkenes	5.00 - 7.69	0
Total Aromatics	24.32 - 32.91	34.20 - 75.63
Total Unidentified	0 - 3.02	0 - 12.8

[1] Data are from Sanders and Maynard (1968) and Runion (1975). The range of numbers are for different grades of gasoline of low, medium, or high octane.

[2] Data are from EPRI (1978). The range of numbers correspond to different amount of hydroprocessing. Increased hydroprocessing results in fuel with a lower aromatic content.

PRODUCT BUILDUP RATES WILL DETERMINE MAGNITUDE OF ENVIRONMENTAL IMPACTS

Once the hazards of synfuels products and byproducts are known, their relative impacts on the environment will depend upon the product buildup rate and market penetration as described for each of the scenarios. All media, air, water and land, must be considered.

Air pollution impacts will occur primarily from the combustion of synfuels in stationary and mobile sources, with some impacts from fugitive emissions occurring during transportation, storage, and handling operations. Under the National Goal Scenario, coal liquids and shale oil products will contribute the greatest percentage of products. A level of 1.4 MMBPD of these fuels will be produced in 1992 and continue through 2000. Coal liquids will most likely be used in all sectors of the market including utilities, transportation, industrial, and commercial. As most of the products will be used in stationary sources, the air pollution impacts are expected to be less than from shale oil products, all of which will be used by transportation sources. The individual mobile sources do not lend themselves to as effective emission controls as centralized stationary sources. Due to the moderate amount of petroleum product use that is expected to be replaced by synthetic liquids, the air pollution impacts are expected to be moderate.

Under the nominal rate scenario (Scenario 2), only 0.5 MMBPD of liquid fuels will be produced in 1992, and the 1.4 MMBPD level will not be reached until 1998. This will provide relatively lower air pollution impacts from liquids combustion than the National Goal Scenario. The use of low- and medium-Btu gas is projected to be higher under scenario 2 than scenario 1, although air pollution impacts are not considered to be significant since these products will most likely be used for in-plant and feedstock applications.

The greatest relative impact would occur under the accelerated rate scenario, as the quantities of each product are higher than for each of the other two scenarios. By 1992, shale oil and coal liquids production reach a level of 1.8 MMBPD and as much as 3.5 MMBPD by 2000. Shale oil in this period is in excess of 0.9 MMBPD, all of which is used in transportation sources. As shale oil products can be used virtually anywhere in the U.S., there is very little of the population that may not be exposed to the combustion products. If the majority of the products are used by the military sector, the geographic area of use may be better defined. Significant market penetration under this scenario will also be made by SNG which may be used in all sectors with the exception of transportation. As this product has widespread application, its composition must be accurately defined to determine if combustion will produce air pollution impacts different from use of natural gas.

Water pollution will occur primarily from spills associated with the transportation of synthetic liquids. As the production of these is greatest under the accelerated rate scenario, it provides the greatest potential for these impacts. The crude and refined shale oils, as well as coal liquids will be transported over long distances by pipelines, and then to the markets by various modes of transportation. The loading of tankers and barges, and transportation of the products by waterways provides a moderate degree of spill potential.

Solid wastes will be generated primarily by the pollution control systems used during synfuels utilization. These systems will be limited to stationary source applications where the coal liquids and gases are used in utilities and for industrial processes. As the quantities of solid wastes produced will be dependent on the amount of these fuels used, it will have the greatest impact under the accelerated rate scenario. Oil shale products will not contribute to these impacts since they will be used in transportation sources. By 1992 under this scenario, coal-derived fuels will be produced at a level of 1.8 MMBPD and 4.1 MMBPD by 2000. The majority of these products will be used in stationary sources with emission control systems producing solid wastes. Under scenario 2, only 1.7 MMBPD of coal-derived fuels will be produced by 2000, and 1.8 MMBPD under the National Goal Scenario. As another example of the need to determine synfuel composition, the solid wastes generated by control systems may contain toxic or hazardous components which upon disposal may leach into groundwaters at waste disposal sites.

On the basis of the information presented, significant data need to be developed to assess control technology options. The optimal method of control, if achievable, would be to upgrade the products to remove as much of the pollutant source content as possible rather than rely on downstream pollution controls. This would have significant benefits on pollution impacts that may occur prior to product utilization. As an example, fugitive emissions into the atmosphere, or spills into waterways would not be expected to be severe if the majority of pollutants were removed during the manufacture of the product.

Once the products are ready for combustion, emission controls will be necessary if product upgrading is unsuccessful. Recent small-scale tests of synfuels combustion have provided encouraging results from an environmental perspective. Several combustion tests of SRC liquids and solids, EDS and H-Coal liquids, shale oil, and coal derived gases have been conducted. For test purposes, some of the combustion devices were not equipped with high-efficiency pollution control devices. Once the products are used in commerce, Best Available Control Technology (BACT) will be required.

EPA is currently proceeding to develop Pollution Control Guidance Documents for all of the synfuel technologies that are being considered under the three scenarios. The purpose of these documents is to foster the development of acceptable synfuels technologies with a minimum of regulatory delays. A similar series of documents may be prepared for the utilization of the products from these technologies.

SIGNIFICANT ENVIRONMENTAL ISSUES FOR SYNFUELS UTILIZATION

- Although a few synfuels products have been included in the toxic substances inventory, most synfuels may be designated as new products under TSCA. EPA will have to identify potential risks associated with the transport and use of synfuels products and by-products, as well as their end uses. Risk and exposure concerns depend on the market infrastructure and likely end use of the variety of products that will result. More diverse end uses and methods of handling, storage, and distribution will increase the exposure potential.

- In addition to TSCA, stipulations of the Clean Air Act will also impact the synfuels market. Atmospheric emissions from fugitive sources are potentially an environmental concern, as well as end-use combustion emissions. These emissions must be characterized so that BACT determinations can be made. Similarities and differences with related petroleum products need to be evaluated.

- Potential atmospheric emissions are much more diverse than the limited set of criteria pollutants which constitute the majority of air pollution concerns today. A critical issue is not so much that hydrocarbons may be an emission, but rather an assessment is needed of the kinds of other organic emissions and the associated risks.

- The potential of accidental spills in the transport and storage of synfuels products and by-products is one of the most critical concerns for protection of groundwater quality and dependent drinking water sources, as stipulated by the Clean Water Act. Additional contamination of receiving waters could be caused by area washdown and stormwater runoff at facilities where minor leakage occurs.

- RCRA requirements will include an integrated solid and hazardous waste management program. Waste oils, storage tank sludges, disposable materials (seals, packing, etc.), and ash residues can all be anticipated from synfuels usage, in addition to waste by-products.

- There is a high probability that synfuels will be blended with petroleum products, either as refinery and petrochemical feeds or as products at end-use locations. EPA will have to judge the applicability of existing regulations covering petroleum product transport and use when the product characterizations are related to blend ratios. Furthermore, synfuels materials that will be used as chemical feedstocks will require environmental assessments regarding their physical, chemical, and biological acceptability.

- The eventual complexity and diversity of the synfuels market infrastructure will represent a challenge to traditional environmental monitoring and inspection procedures, as well as control technology assessment.

- Some of the control approaches will be equipment and operations oriented. This characteristic will require a close EPA interface with other regulatory agencies (such as DOT, ICC, and Coast Guard) regarding transportation operations which are both safe and environmentally acceptable.

- The feasibility of segregating the handling and end-use of potentially hazardous synfuels will certainly have to be evaluated. Proper assessment of environmental risks from synfuels product end-use will be needed to establish exposure estimates.

PERMITTING AND PROGRESS

EPA's regulatory role in an emerging synfuels market will involve permitting for the production, storage, transportation, and end use of the products. Permitting procedures will have to be streamlined to eliminate unnecessary delays in the long-range national goal of reducing petroleum imports. TSCA requirements will be particularly critical in this emerging industry. Plans have been announced by some industries to begin construction of plants to supply SNG and chemical feedstocks. Synfuels projects scheduled for the mid-1980s include shale oil development in Colorado and Utah, and the SRC II demonstration plant in West Virginia. With typical engineering and design efforts requiring 2 years, and construction another 2 to 3 years, it is essential that all permitting be complete within 1 year to keep these critical developments on schedule.

Session III: ENVIRONMENTAL ASSESSMENT: GASIFICATION AND INDIRECT LIQUEFACTION

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ENVIRONMENTAL TEST RESULTS
FROM
COAL GASIFICATION PILOT PLANTS

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Environmental awareness and the world oil situation are having a profound impact on the U.S. Electric Power Industry. "Environmental acceptability" has been redefined and it is emerging as one of the major criteria for selection of a power generation process to satisfy increasing load demand or to replace retired units. Furthermore, the fact that the cost of fuel has risen in real terms dictates that more fuel efficient plant configurations will be deployed. Fuel efficiency and environmental tolerability come only at the expense of increased monetary cost.

These fundamental changes certainly are creating problems for the power industry but they are also creating opportunities for new and more appropriate power generation processes.

EPRI has high expectations that combined cycle power systems fueled by gas from coal will be cleaner and more efficient than the competing processes for equivalent capital cost. Advantages accrue to these Gasification-Combined Cycle (GCC) systems primarily from the relative ease of cleaning fuel gas, the benign nature of the waste products, and the inherent and proven high thermodynamic efficiency of the combined cycle configuration.

These and other advantages will be discussed. Coal gasification processes will be identified which most effectively capitalize on these advantages. Environmental test results on these processes will be summarized. Finally, the plans for commercial scale demonstration of a GCC system will be reviewed. This demonstration will be a critical milestone since no technology can be considered to be a real option until it has been operated at an appropriate scale.

ENVIRONMENTAL TEST RESULTS
FROM
COAL GASIFICATION PILOT PLANTS

INTRODUCTION

The combined circumstances of rapidly escalating oil prices, reduced availability of oil and natural gas, strict plant emission standards and the prospect of continued delays in nuclear implementation plans, provide the electric power industry with urgent incentives to develop economically competitive and environmentally acceptable new methods of power generation based on our most plentiful fossil fuel resource - coal.

Of all these motivations, it is probably the environmental aspects which constitute the major incentive for coal gasification based power systems, since without the requirement for post-combustion clean up of the flue gases it would clearly be less costly to simply burn coal directly.

Coal gasification based systems offer distinct environmental advantages over conventional direct coal fired plants with flue gas clean up, since emission forming constituents are removed prior to the combustion process. When coupled with combined cycle power generation the resultant Integrated Gasification Combined Cycle (IGCC) plants will be more efficient and use less water than direct coal fired units. Studies show that such IGCC plants when designed to current emission standards and using currently commercial combustion turbines are economically competitive with direct coal firing. If emission standards become more restrictive the competitive position of IGCC technology will be further enhanced. There are also considerable prospects for future improvements in both coal gasification and combustion turbine technology, which will enable the industry to resume its historic learning curve for more efficient less costly systems.

EPRI CLEAN GASEOUS FUELS PROGRAM

The overall goal of the EPRI Clean Gaseous Fuels Program is to develop economically competitive and environmentally acceptable coal gasification-based generating systems.

The principal technical objective of the EPRI program is to design and operate an integrated Texaco entrained gasification-combined cycle demonstration plant of about 100 MW by 1985. A second demonstration plant based on another gasifier is also planned. The program also includes work to improve gasifiers, gas clean-up technology, heat recovery boilers, fuel gas combustors and other components of gasification-based generating systems.

Coal gasifiers react coal, steam and air or oxygen to produce a gaseous fuel, primarily carbon monoxide and hydrogen. The sulfur in the coal is converted to hydrogen sulfide (H_2S), which can be removed from the gas and converted to elemental sulfur by processes currently used widely in the natural gas, chemical and petroleum industries. The mineral matter is withdrawn primarily as ash or slag from the gasifier or from the gas stream as part of the gas cleaning process. The coal nitrogen is converted either to ammonia, which can readily be scrubbed from the gas, or to nitrogen itself.

Gasifiers are also important components of other coal conversion technologies of potential benefit to utilities. The CO-H_2 product gas can be catalytically converted to methanol for use in peaking or intermediate service. Gasifiers can be used to provide hydrogen for use in Exxon, H-Coal or SRC coal liquefaction plants by gasifying the liquefaction residues.

ECONOMIC ATTRACTIVENESS OF GCC PLANTS

EPRI studies show that integrated gasification combined cycles using commercially available combustion turbines (2000°F inlet temperature) and based on Texaco or BGC/Lurgi slagging gasifiers are competitive with conventional coal-fired power plants with stack gas cleanup. Table 1 shows a performance comparison between conventional coal firing and gasification-based power systems. The data presented in this table reflect 1978 environmental control regulations. Cost estimates are included for cycles with advanced high temperature turbines to illustrate the further performance improvement potential of this technology. As environmental control regulations become more stringent, the economic advantages of gasification combined cycle (GCC) power plants will increase markedly. Table 2 shows estimated costs for more stringent projected mid-1980s standards. GCC systems offer better efficiency, lower emissions, reduced water consumption and land requirements, less fuel and chemicals consumption, and reduced solid waste volume. The solid waste from the Texaco, BGC/Lurgi slagger, and Combustion Engineering gasifiers is in the form of extremely inert slag which should be readily disposable at lower cost than solid waste from a coal-fired plant.

Gasification may also offer fuel for retrofit to existing gas and oil-fired boilers, combined cycles and combustion turbines. Gasifiers might be installed in an existing plant or in some cases remotely, with fuel distributed by pipeline. Gasification may allow repowering existing boilers with combustion turbines to reduce the heat rate and provide increased generation capacity in convenient increments at an existing site with probably reduced permitting periods.

ENVIRONMENTAL ADVANTAGES OF GASIFICATION-BASED POWER PLANTS

The potential environmental advantages of gasification-combined cycle power plants over direct coal fired plants with flue gas cleanup are summarized in Table 3. GCC plants offer better resource utilization - more kilowatts per ton of coal mined, less water usage per kilowatt, and less land since sludge disposal is not required. They are also capable of achieving markedly reduced emissions compared to direct coal fired units. Each of these aspects is discussed in more detail below.

Resource Utilization

GCC systems utilizing currently available combustion turbines offer a minor but measurable improvement in heat rate over conventional coal plants with scrubbers. However, better efficiencies projected for GCC plants with higher temperature turbines currently being developed, i.e., machines capable of operating at firing temperatures above 2000°F upwards to 2600°F, should result in significant reductions in coal use versus direct coal-based units of similar capacity as reflected in the range of coal consumption estimates for GCC plants in Table 3.

Table 1 SUMMARY OF PRESENT AND PROJECTED

GCC SYSTEM PERFORMANCE

1978 FEDERAL EMISSION CONTROL REQUIREMENTS

	Coal Fired Plant	Texaco GCC 2000°F Turbine	Texaco GCC 2600°F Turbine	BGC Slagger GCC 2600°F Turbine
Heat Rate, Btu/kWh	9900	9500	8460	7920
Capital Requirement, $/kW	900	860	830	690
30-Year Levelized Cost of Electricity, mills/kWh	57.5	51.1	47.9	41.3

Basis: mid-1978 dollars; high-sulfur Illinois coal; coal cost $1.00/million Btu; 70% capacity factor.

Table 2 ECONOMIC COMPARISON OF TEXACO GASIFICATION-BASED POWER SYSTEMS USING CURRENT (2000° F) COMBUSTION TURBINES WITH CONVENTIONAL COAL-FIRED STEAM PLANTS EMPLOYING WET SCRUBBING OF STACK GASES.

	1978 Federal Emission Controls		Projected mid-1980's Emission Controls	
	Coal Fired	Texaco GCC	Coal Fired	Texaco GCC
Heat Rate, Btu/kWh	9900	9500	9950	9680
Capital Requirement, $/kW	900	860	1180	900
30-Year Levelized Cost of Electricity, mills/kWh	57.5	51.1	69.0	52.9

Basis: mid-1978 dollars; high-sulfur Illinois coal; coal cost $1.00/million Btu; 70% capacity factor.

Emission Controls	1978	mid-1980's
sulfur	85% removal	95% removal
particulates	0.03 lbs/10^6 Btu	0.02 lbs/10^6 Btu
NO_x	0.6 lbs/10^6 Btu	0.2 lbs/10^6 Btu
waste water	---	zero discharge
coal ash	---	special handling

Table 3 RELATIVE ENVIRONMENTAL EFFECTS/RESOURCE REQUIREMENTS

1000 MW POWER PLANTS

	PC Boiler with Wet Scrubber	GCC Plant
Coal Consumption - lbs./kWh	0.80	0.64-0.77
Limestone Required - lbs./kWh	0.12-0.15	-
SO_2 Emissions - ppm	80-400	50-225
NO_x Emissions - ppm	300-500	40-90
Particulate Emissions - lbs./10^6 Btu	0.03	<0.02
Make-up Water - gal./kWh	0.6-0.65	0.45-0.55
Land Required - acres	1200-2400	200-500

Note: Solid wastes, consisting of sulfur and inert slag, produced in GCC plants in significantly lower quantity than troublesome scrubber sludge produced in coal fired unit.

Also, while power produced in conventional coal plants is derived from steam turbine generators, a large part of the electricity output of GCC plants is developed directly from fuel combustion energy with the remainder being produced in a steam cycle. Accordingly, make-up water requirements (by far the major part of which supports the cooling water system for the steam turbine generator condenser) are significantly less in GCC plants.

Sulfur Emissions and Disposal Land Required

The range of sulfur emissions cited in Table 3 is based on single stage sulfur removal from high and low sulfur coal based systems for both the coal fired boiler and gasification combined cycle power plant. Sulfur emissions can be reduced at additional expense by adding a second stage of stack gas scrubbing to the coal fired boiler plant or by several mechanisms in the coal gasification based plant. EPRI economic evaluations have shown that incremental sulfur removal from gasification based systems is less expensive than from coal fired boiler plants. Additionally, gasification based systems will produce elemental sulfur and inert slag, potentially saleable byproducts, while the coal fired boiler produces a much larger volume of waste sludge which contributes significantly to the additional disposal land required for the latter option.

NO_x

In coal or oil combustion, NO_x is produced by two mechanisms, the oxidation of nitrogen in the fuel (fuel NO_x), and oxidation of nitrogen in the combustion air (thermal NO_x). Fuel NO_x can account for up to 75% of the total NO_x emissions from a coal fired plant. This is not the case with coal gasification based power plants because the coal-bound nitrogen leaves the gasifier as either N_2 or NH_3 which is scrubbed out in all commercial or proposed processes. The issue then becomes one of controlling thermal NO_x by limiting temperature via steam/water injection and/or phased combustion techniques. At Texaco's Montebello pilot plant, EPRI has burned medium Btu gas in existing and developmental gas turbine combustors with promising results[1] (at atmospheric pressure). A 70 to 80% reduction in NO_x emissions over conventional pulverized coal fired power plants should be achievable with gasification-combined cycle power plants.

Particulates

There will be for various reasons, minimal particulate emissions to the atmosphere from gasification based power plants. Gasification systems, specifically those supported by EPRI, propose at least two sequential intensive gas scrubbing steps. Isokinetic sampling at Texaco's Montebello pilot plant and the Westfield Development Centre of the British Gas Corporation has failed to detect any significant particulates after scrubbing. For combined cycle systems, particulate levels in gas turbine fuel must be minimized to prevent erosion or deposition on gas turbine blades. For mechanical integrity of these systems, if for no other reason, particulates will be minimized.

Soot formation can occur in pulverized coal fired systems and oil fired systems, especially during transients or upsets. Soot formation is not expected to be a problem with coal gas based systems because of the burning characteristics of the gas and better controllability of the fuel/air ratio.

Non-Leachable Slag

EPRI actively supports 3 gasifiers, all of which are slagging gasifiers, that is, they are operated above the melting temperature of the coal mineral matter so it is extracted in the form of a glassy inert frit. This slagging mode of operation has two distinct advantages:

1. Operating at higher temperature speeds the gasification reactions leading to greater throughput per reactor and reduced waste of reactants (e.g., gasification steam).
2. Slag is environmentally more acceptable than ash.

The EPA proposed Waste Extraction Procedure (among several others) has been performed on the slags produced in all three gasifiers which EPRI supports, BGC/Lurgi Slagger, Texaco, and Combustion Engineering. Although the slags were produced from a variety of coals, the maximum concentrations of toxic elements in the leachate, or often the minimum limits of detection with the available equipment, are shown in Table 4. In no case did the trace element concentration in the leachate approach the EPA proposed criteria for hazardous wastes which is 100 times the drinking water standard. When more sensitive detection equipment was used, the actual concentrations were most often much lower than those shown in the table. Those elements with proposed limits greater than 5000 ppb have been omitted from the table since in all cases, their concentrations in the leachate actually comfortably met the drinking water standard.

One preliminary comparison has been made between a gasifier slag and fly ash from a coal fired boiler based on coals with similar ash compositions. This effort was conducted by Oak Ridge National Laboratory under contract to EPRI and examined the leachates on solid wastes from a conventional wet bottom slagging boiler and the Combustion Engineering pilot plant gasifier. The fly ash leachate generally had 10 to 1000 times greater concentrations of toxic elements than the gasifier slag leachate (the narrowest margin was 2 times). The slag from slagging gasifiers therefore appear to be environmentally tolerable, certainly more so than fly ash.

GASIFIER SELECTION FOR ELECTRIC POWER APPLICATIONS

Coal gasification is almost as old as the industrial revolution itself, serving a wide variety of industrial applications from steel, refining, chemicals, to fuel and power production. Perhaps it is for this reason there are so many coal gasification processes currently under development. A recent Oak Ridge National Laboratory survey lists almost 100 such projects.

A first priority at the outset of the EPRI gasification program was the establishment of criteria for selection of those processes most likely to meet the requirements of the power industry. Coincidentally, objective criteria were required to evaluate the status of process development for each concept and to assess the risk and benefit involved at each scaleup stage. The attached Table 5 summarizes EPRI Program Criteria for scaleup to the demonstration size of 1000 tons/day of coal per unit, a size judged sufficient for subsequent commercial deployment.

The electric power industry emphasizes the need for plant reliability and availability. Therefore, simplicity of design with inherent ease of maintenance is very desirable. The preferred gasification process should be

Table 4 GASIFIER SLAG LEACHING TESTS

	Proposed EPA Limit ppb	Gasifier Slag Leachates ppb
As	5000	< 200
Cd	1000	< 10
Pb	5000	< 140
Mn	5000	< 250
Hg	200	< 2
Se	1000	< 80
Ag	5000	< 20
Cr	5000	< 20

Table 5 CRITERIA USED IN COAL GASIFICATION TECHNOLOGY SELECTION FOR SCALE UP TO DEMONSTRATION SIZE (≈1000 TPD COAL) IN THE ELECTRIC POWER INDUSTRY

- Simplicity
- Feedstock flexibility
- Complete carbon conversion
- Absence of troublesome byproducts
- Compatibility with power generation requirements
- Existence of an operating pilot plant of greater than 100 tpd coal capacity
- Proof (direct experimental evidence) of all essential aspects of the process with regard to the above criteria including waste heat recovery and gas clean up

flexible with regard to coal feed properties and should be able to convert all the carbon to gas. Incomplete conversion or the formation of byproduct tar gives rise to additional processing complications, disposal problems and the potential for greater environmental intrusion. The process must also be compatible with the power generating system needs. This implies a rapid response rate for ease of load change, a wide operating range, and a relatively constant heating value of the product gas throughout the operating range and during transients. For scaleup to demonstration size, all essential aspects of the process should have been experimentally proven on a large pilot plant of 100 tons/day capacity (so that eventual scaleup is less than tenfold). Since the gasifier is only one part of a large system, such a pilot plant should also verify the technical concepts for the waste heat recovery and gas clean up systems.

When these criteria of simplicity, flexibility, cleanliness,etc. are examined against the known characteristics of the three main types of gasifier - moving bed (both dry ash and slagging), fluid bed and entrained systems, it is clear that entrained systems come closest to meeting the desired criteria. Coincidentally three such systems - the Texaco, Shell-Koppers and Combustion Engineering, have each progressed to an advanced state of development and pilot plants greater than 100 tons/day coal capacity are currently being operated for each of these technologies. Each of these developments is able to draw on a background of commercial gasification experience, and each of these organizations plans to scale up the pilot plant to commercial size demonstration units of about 1000 tons/day coal capacity.

Each of these three entrained systems offer distinct environmental advantages in their demonstrated complete carbon conversion,production of a dense inert slag, and absence of tar and other troublesome byproducts.

The currently commercial Koppers-Totzek process has similar environmental advantages although low throughput, as yet incomplete carbon conversion and atmospheric pressure indicate higher costs than the other three entrained systems referred to above.

The current commercial Lurgi moving bed gasifier operates with dry ash removal, and excess steam is injected at the bottom to keep the ash below slagging temperature. This excess steam requirement reduces the thermal efficiency and produces large volumes of contaminated water which require treatment. The British Gas Corporation (BGC) is developing a slagging version of the Lurgi gasifier at Westfield, Scotland. By operating at the higher slagging temperature , essentially only the steam for the gasification reaction is required. The steam consumption and overall efficiency is greatly improved, and the waste water treatment requirements markedly reduced.

Both dry ash and slagging versions, being countercurrent devices, operate at lower outlet temperatures and the outlet gases thereby contain tars, oils and phenols. The slagging version provides a means for their subsequent gasification by injection into the slagging region, so no net tar production will result. Lurgi is also working on various recycle schemes to consume the tars and liquors.

The existence of tars does create additional processing and increased safety and housekeeping requirements. However, such a choice can be justified if the overall economics justify the extra costs for environmental acceptability. Processes operating in the slagging region do offer the opportunity for recycle and consumption of streams with fuel value, and a means of recycle of contaminated water streams (perhaps with coal added as a slurry) so as to capture the minerals in the slag.

The only currently commercial fluid bed gasifier, the Winkler, has historically suffered from four problems - feeding caking coal, tar production (with bituminous coals), high carbon in the ash, and inability to consume fines. The 'U' Gas and Westinghouse small pilot plants (< 1 ton/hour) seem to have been able to solve the caking coal and tar production problems at least in short runs. By operating with a specially designed ash - agglomerating zone at the bottom, ash low in carbon has been observed, however, full consumption of fines has yet to be demonstrated. With the smaller scale of current experimentation, we judge the scale-up risks, particularly with the ash agglomerating zone, to be greater than with the entrained systems. In addition there is still some concern as to whether tar formation can be avoided during the load change and start up conditions expected for a gasifier operating in a power plant.

EPRI TEST RESULTS FROM COAL GASIFICATION PILOT PLANTS

The tests conducted to date on coal gasification pilot plants give reason for optimism that environmentally acceptable commercial power plants can be designed to economically meet current and proposed emission standards. However, it must be admitted that in many cases the configuration of the pilot plants and the short run lengths inevitably associated with pre-commercial facilities, do not lead to results directly translatable to larger continuously operating plants with full economic use of recycle steams

At EPRI the overall program is aimed at obtaining process and environmental data on several gasification processes judged to be at a stage of development where commercial deployment can reasonably be projected in the 1980's. These studies are planned, wherever possible, at larger pilot plants (e.g., BGC/Lurgi at Westfield, Texaco at Oberhausen, and Combustion Engineering at Windsor, Connecticut) during runs of sufficient length to accommodate appropriate recycle of process streams.

Comparison of the environmental impact of various coal technologies in the trace element area is particularly difficult.

Coal is variable, not only from mine to mine in a large deposit, but even within a given mine, particularly with regard to variation in the mineral matter content.

To obtain consistent comparisons of direct coal firing, fluid bed combustion and coal gasification presents a great challenge requiring an extremely rigorous set of long term tests on the technologies with careful monitoring of feedstocks. Too often comparisons are made with different coals, unrepresentative plants, short runs, etc.

EPRI has supported and is supporting test programs on the BGC/Lurgi, Combustion Engineering and Texaco technologies. We are also working with Shell-Koppers. All of these processes produce the ash as a dense slag and offer recycle opportunities.

BGC/Lurgi Slagging Gasifier

Being a slagging gasifier, the BGC/Lurgi Slagger produces all the coal mineral matter as an inert glassy frit. Under the DOE's high Btu demonstration program, tests on U.S. coals were conducted at BGC's Westfield pilot plant to determine performance and to characterize emissions. Based on the slag leaching test results, the EPA in Ohio (proposed site of the Demonstration Plant) has agreed that the slag is a non-hazardous waste.

The Slagger is a countercurrent moving bed gasifier, and therefore tars are present in the raw product gas. As indicated by the Kosovo tests (the subject of a paper to be presented later in this meeting), the presence of tars dictates that a great deal of attention must be paid to plant design and procedures to prevent worker exposure to these compounds. The Slagger can in all cases easily accommodate complete gasification (destruction) of these tars as successfully demonstrated under the EPRI test program (on Pittsburgh No. 8 coal) at the Westfield 350 tpd pilot plant in late 1979. The tars are therefore only a plant internal recycle stream and need not intrude into the outside environment. Another advantage of the Slagger over the dry ash Lurgi type gasifiers tested at Kosovo is that the Slagger normally consumes 80-90% less steam, dramatically reducing the hydrocarbon-saturated wastewater stream. Conventional wastewater treatment of this stream to acceptable limits hence becomes a much more manageable endeavor. Also, since this stream is so small the possibility exists of using it to slurry finely ground coal to an entrained gasifier such as Texaco thus utilizing all the hydrocarbon content of the feed coal and further simplifying the task of water treatment.

EPRI's economic evaluations of the BGC Slagger show it to be very promising and therefore worth the extra effort needed to deal with the tars in an environmentally acceptable manner. The Pipeline Gas Demonstration Plant planned for Ohio will hopefully verify this acceptability without reducing its economic viability. An extensive environmental program has already been specified for this project.

Combustion Engineering

The C-E gasifier has most of the previously cited environmental advantages of entrained gasifiers over coal fired boilers including non-leachable slag, no detected hydrocarbon production, minimum particulate, NO_x, SO_2 effluents, and reduced waste disposal land requirements. Since it operates at atmospheric pressure, the C-E gasifier is economically attractive for oil or natural gas fired boiler retrofit to conserve these valuable resources. In such applications, however, water consumption would be as great as that in a conventional coal-fired boiler plant. Combined cycle power plants based on the C-E gasifier also appear competitive with direct coal firing, with advantages of reduced water consumption and relatively low cost sulfur removal.

A comprehensive program is planned under EPRI sponsorship to measure gaseous emissions plus liquid and solid effluents from the Process Development Unit (PDU) gasifier at Windsor, Connecticut. At a design capacity of 120 tons of coal per day, it is currently the largest operating gasifier in the U.S.

An effort is underway by Oak Ridge National Lab (ORNL) to compare wastes from the gasification process with those of a direct coal-based power plant using similar coal feedstock. The first results are very tentative because the gasifier has not achieved well-balanced full-scale operation; nevertheless, they are very encouraging. For example, solids leaching tests on gasifier slag point to very low concentrations of selected metals relative to proposed standards. Results of combustion plant bottom ash were comparable. However, the fly ash showed 10 - 1000 times the concentration of some toxic elements. This appears consistent with expectations of an environmentally acceptable solid waste from high temperature, entrained-flow gasifiers, i.e., in the form of chemically inert slag particles.

In the EPRI-funded effort Radian Corporation is preparing to conduct an extensive sampling program to assess both organic and inorganic emissions, with emphasis on potentially hazardous components. The methodology developed here may also form the basis for future environmental assessment of other prominent gasification technologies.

Texaco Process - Montebello Pilot Plant

In the wake of the 1973 oil embargo, Texaco undertook a concerted effort to advance the development of its coal gasification process. This technology had been first tested in the 1950's as an outgrowth of Texaco's successful partial oxidation process for producing synthesis gas from heavy oils and natural gas. In the last 5 or 6 years a large number of coals and other solid feedstocks, including petroleum coke and coal liquefaction residue, have been tested with considerable success in a 15 tpd pilot plant at the Montebello Research Laboratory near Los Angeles. Among these tests, particularly in the most recent 2 year period, have been efforts which have emphasized in significant detail the environmental aspects of the process. The equipment configuration at Montebello is shown in the attached flow sketch, Figure 1.

In a continuing set of EPRI-sponsored runs at the Montebello unit utilizing Illinois No. 6 coal as the feed and employing as the oxidant both oxygen and, alternatively, oxygen-enriched air (35% O_2), very encouraging operational and environmental results have been obtained. The Texaco gasifier was shown to be particularly responsive, reacting essentially instantaneously to rapid changes in throughput. The product gas composition remained virtually unchanged at various load levels and even during fast transients. One major inherent environmental advantage of the Texaco process over most other gasifiers was confirmed as expected in that no undesirable liquors or tars were produced. These byproducts, when formed in other processes, usually appear in the waste water streams, creating a substantial removal and disposal problem. At the high reaction temperature of the Texaco gasifier (2300 to 2800°F), such condensable materials are unstable and are destroyed.

The Selexol® sulfur removal system, when operating within its design specification, removed upwards of 98 percent of the H_2S in the gas. The only other significant sulfur species present was COS, measured in the feed gas to the Selexol® unit at about 5 percent of the H_2S level, and 50 percent of this COS was removed. It is believed that if required, the COS level could be further reduced by catalytic hydrolysis to H_2S ahead of the acid gas absorber.

It should be noted that the Selexol® process installed at Montebello is among the acid gas removal alternatives likely to be preferentially applied in eventual commercial gasification-combined cycle plants due to its selectivity in removing H_2S versus CO_2. For gas turbine applications the latter compound, CO_2, can remain in the gas and contribute, in the form of increased mass flow, to the total energy developed.

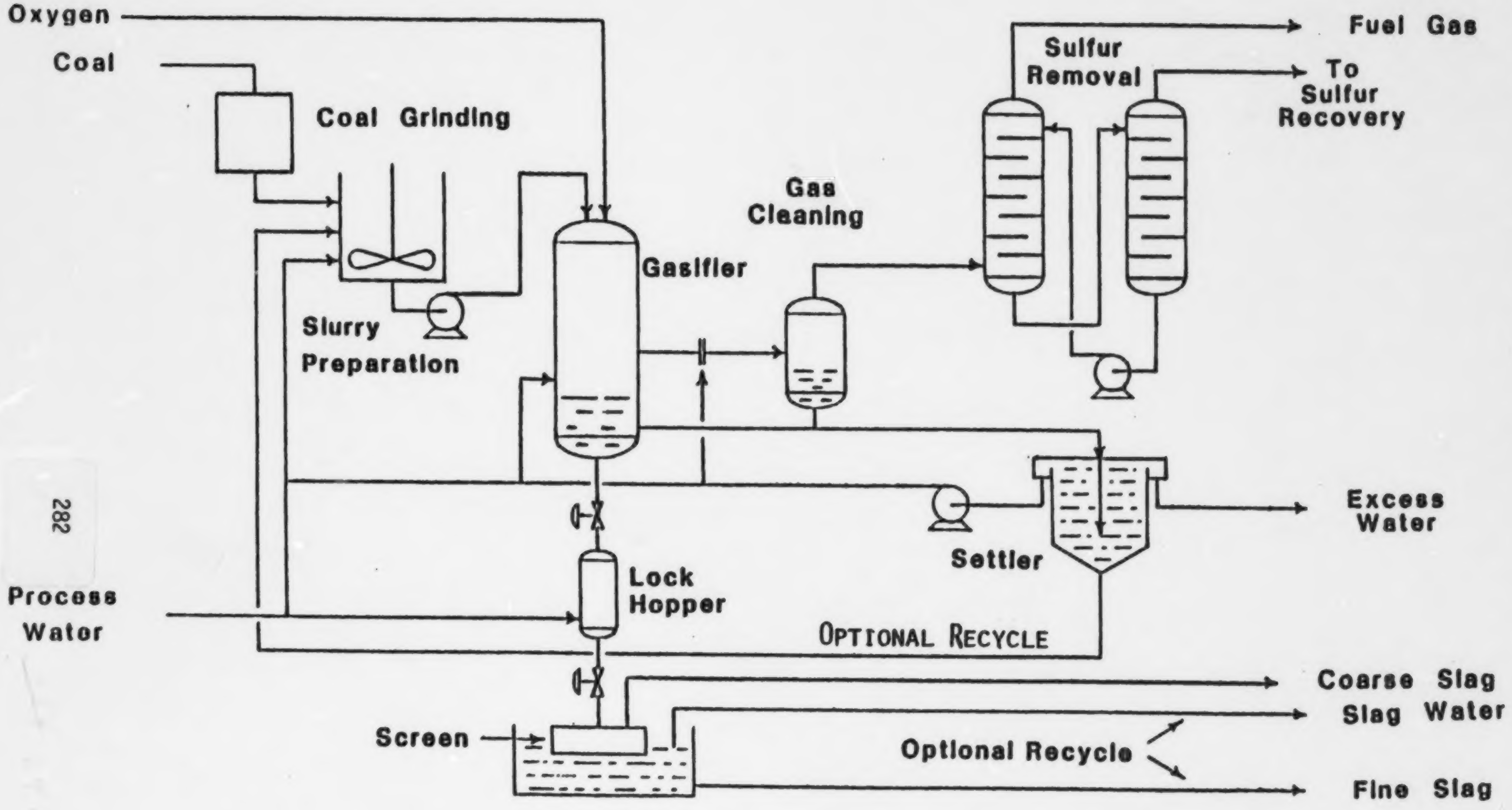
Oxygen
Coal
Coal Grinding
Slurry Preparation
Gasifier
Gas Cleaning
Sulfur Removal
Fuel Gas
To Sulfur Recovery
Excess Water
Settler
Lock Hopper
Process Water
OPTIONAL RECYCLE
Screen
Coarse Slag
Slag Water
Optional Recycle
Fine Slag

Figure 1 Schematic flow diagram - Texaco Coal Gasification Process - Montebello 15 tpd pilot plant.

In the EPRI-funded test runs, particulate levels in the product gas were essentially negligible, i.e., less than 0.1 mg per normal cubic meter. The ammonia level in the gas was less than 1 ppm. In addition to the product gas, analytical data were gathered in the EPRI runs to determine the constituents of various other plant streams, including the presence and nature of trace materials. With the exception of benzene, organic compounds on the EPA priority pollutant list were not detected in the effluent and recycle water streams at the 10 ppb level. Benzene was detected at a level of less than 20 ppb in the recycle water. No polynuclear aromatics (PNA's) which appear on the EPA priority pollutant list were found in the slag or particulates. Leaching tests conducted on the slag indicated all trace metals found in the leachate fell at least an order of magnitude below the one hundred times EPA drinking water standard proposed for implementation of the Resource Conservation and Recovery Act. In fact, all but three trace metals actually met the drinking water criteria, and these three were present at less than ten times the drinking water standard.

A similar level of environmental analysis and testing to that discussed above has been conducted by Texaco at the Montebello facility on a western coal, Kaiparowits. Reference No.2 in the list at the end of this paper contains a detailed discussion of coal, gas, water, slag, and slag leachate compositions in both the EPRI-sponsored Illinois No. 6 coal tests and the Kaiparowits coal tests.

Larger Texaco Pilot Scale Facilities

Extensive testing, including substantial environmental analysis, is planned to be carried out in larger Texaco gasification facilities now operating or scheduled to commence operation soon. EPRI is proceeding with plans to conduct during the next few months testing of Illinois No. 6 coal in a 150 tpd Texaco unit in West Germany. These runs will be of similar scope to the oxygen-blown runs performed at Montebello and the coal has been procured from the same mine. This larger unit, operated at Oberhausen by Ruhrchemie (a European chemical firm) to produce synthesis gas for a chemical feedstock, has achieved considerable success in a planned test program on German coals since its start-up in early 1978. Unlike the Montebello pilot plant, the Ruhrchemie facility is equipped with a waste heat boiler, a key component required for efficient gasification-combined cycle power applications. This factor (versus direct water quench for cooling of the gas as employed at Montebello), along with the larger equipment sizes in the German unit, should increase the relevancy of the environmental measurements taken to the projected performance of commercial scale Texaco-based GCC plants. It is intended to perform a careful analysis of the EPRI results from Oberhausen when available to clearly identify the reasons for any significant difference from the Montebello tests, i.e., effects of scale-up, dissimilarities in equipment design or configuration, differing operating conditions, etc.

Another Texaco gasifier, having a capacity of about 200 tpd of coal is being readied for start-up by TVA at Muscle Shoals, Alabama. This plant, designed to produce a medium-Btu gas as feedstock for ammonia synthesis, was the subject of a paper presented earlier at this meeting. It is understood that a comprehensive environmental program is planned for the TVA unit, which utilizes a direct water quench for cooling of the product gas and, accordingly, should be reasonably representative of a number of other industrial applications of the Texaco gasifier.

COOL WATER DEMONSTRATION PROJECT

A number of major energy technology developers and supporters, including EPRI, are proceeding with a project to design, construct, and operate a demonstration scale (commercial size equipment) GCC power plant at Southern California Edison's existing Cool Water generating station. The demonstration unit will integrate a 1000 tpd Texaco coal gasifier with a 100 MW combined combustion turbine-steam turbine electric generating system. The plant flow scheme is depicted in Figure 2 and the project is presently in the beginning stages of detailed design. A preliminary estimate of the product gas composition based on the conceptual design of the Cool Water facility[3] is provided in Table 6. The makeup of the clean gas presented in the table reflects the design criteria of 97 percent removal of the sulfur in the raw gas based on a feed coal containing 0.7% sulfur by weight. Similar (and higher) levels of sulfur removal are quite readily achievable in plants feeding higher sulfur coals through appropriate selection of design options within one of several commercially available acid gas removal processes.

The preliminary expected emissions from the Cool Water plant are shown in Table 7. The projection of SO_2 emissions is based on the clean gas composition in the previous table. It should be noted that the NO_x emissions shown, which correspond to approximately 43 ppm, reflect compliance with the plant permit conditions which apply to the area in California where the plant is to be situated. This criteria is significantly more strict than the federal New Source Performance Standard for stationary gas turbines which limits NO_x emissions to 75 ppm. To achieve the required low NO_x emissions level the project intends to employ gas saturation/steam injection prior to combustion, along with the use of advanced combustor design undergoing development concurrent with the design effort for the plant facilities.

The good performance anticipated regarding particulate emissions is a result of effective water scrubbing of the product gas which is carried out as an integral part of the Texaco gasification process. The use of enclosed storage and dust suppression techniques in the coal receiving, transfer, and preparation areas will, in addition, provide appropriate control of potential emissions from these areas.

In the gasifier process section all but a relatively small amount of the water will be recycled internally. The small amount of process blowdown will be routed along with cooling tower blowdown and other minor power plant aqueous effluents to a lined evaporation pond located on-site. The slag produced will also be stored on-site in an impervious lined storage area, at least until such time as sufficient data has been collected to confirm that, as expected, this material is non-hazardous and alternate off-site disposal (or practical use) can be pursued.

Sulfur produced in the plant as a by-product will be stored at the facility unless and until an application has been developed for it.

The Cool Water project has already received the required State environmental permit from the California Energy Commission (CEC). The conditions of the permit granted by the CEC require that an extensive environmental monitoring and surveillance plan be carried out during the plant operations and test period. The details of this plan are currently being developed.

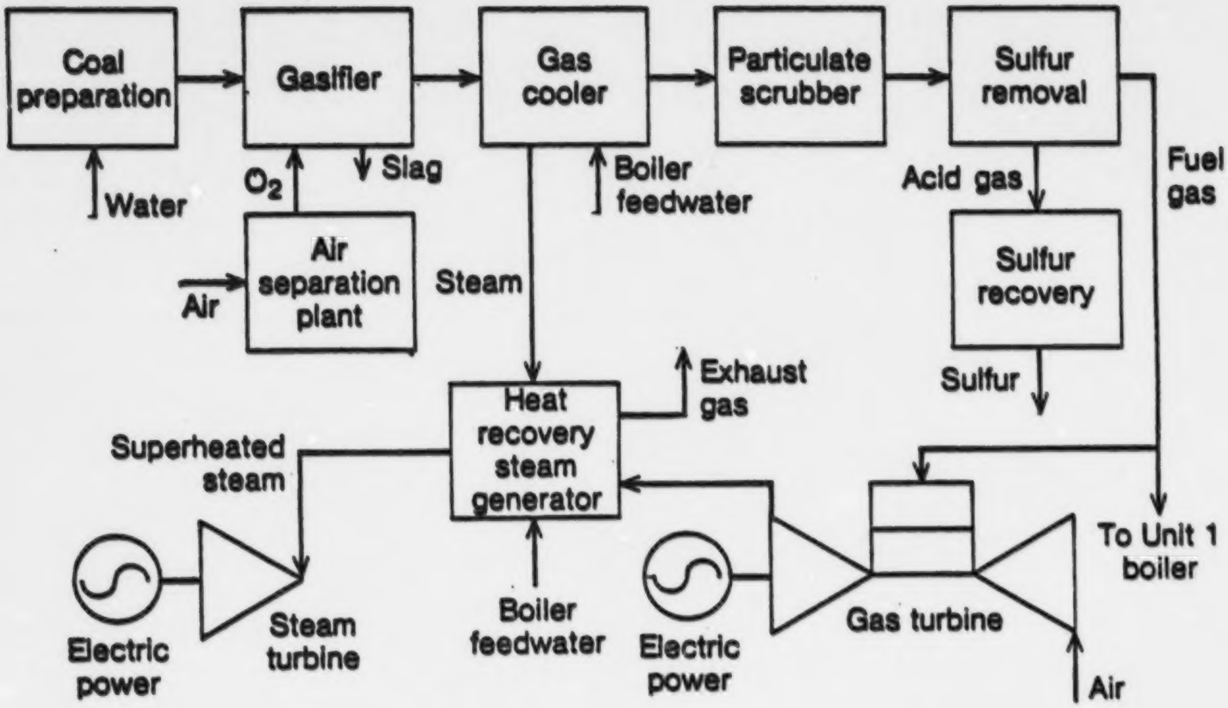
Coal preparation
Gasifier
Gas cooler
Particulate scrubber
Sulfur removal
Water
O_2
Slag
Boiler feedwater
Acid gas
Fuel gas
Air
Air separation plant
Steam
Sulfur recovery
Exhaust gas
Sulfur
Heat recovery steam generator
Superheated steam
To Unit 1 boiler
Steam turbine
Boiler feedwater
Gas turbine
Electric power
Electric power
Air

Figure 2 Block flow diagram for Cool Water project

Table 6 COOL WATER GCC DEMONSTRATION PROJECT

PRELIMINARY ESTIMATED GAS COMPOSITIONS (DRY)

FROM A CANDIDATE WESTERN DESIGN COAL

Component	Vol. Percent	
	Raw Gas	Clean Gas
H_2	33.61	35.94
CO	48.22	51.51
CO_2	17.38	11.86
CH_4	0.09	0.10
N_2 + Ar	0.54	0.58
H_2S	0.15	13 ppmv
COS	0.01	40 ppmv

Table 7 COOL WATER EXPECTED EMISSIONS

	Lbs./10^6 Btu (Coal)
SO_2	0.04
NO_x	0.14
Particulates	0.005

Notes:

1. Emissions based on performance calculations for a candidate (western) design coal.
2. Aqueous effluent intended to be routed to lined evaporation pond.
3. Solid wastes (slag) to be stored at site.

A one-year monitoring program to provide additional data regarding the present local environment in the vicinity of the plant site is nearly complete. The data from this effort, undertaken to comply with regulations promulgated for implementation of the Prevention of Significant Deterioration (PSD) provisions of the Clean Air Act Amendments, will be submitted to the EPA to support the recently prepared project application for a PSD permit.

SUMMARY

The data from existing pilot plants enables us to identify the species, i.e., compounds, present in the various gasification process streams. These species would not be expected to change in scaled-up commercial facilities. What remains unclear, however, is the concentration at which these substances will appear in commercial plants employing recycle of certain materials and other design dissimilarities for continuous economic operation.

The promise of the data obtained so far strongly suggests that process schemes to meet present and future emissions and effluent standards can be economically achieved with coal gasification combined cycle power plants. Nevertheless the detailed long term environmental impacts and full achievement of the above promise can only be obtained by continuous long term operation of a commercial sized (and configured) demonstration plant. It is with this very much in mind that EPRI together with Southern California Edison, Texaco, G.E. and Bechtel have commenced engineering the 100MW gasification combined cycle demonstration plant at Cool Water.

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COS-H_2S RELATIONSHIPS IN PROCESSES PRODUCING LOW/MEDIUM-BTU GAS*

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ABSTRACT

The chemical aspects of the distribution of sulfur between H_2S and COS in the product gas from the gasification of coal are examined. Comparing actual gasifier measurements with equilibrium computations we find that the gas stream becomes frozen corresponding to equilibrium values at high temperature, most likely corresponding to the reactor exit. This implies a sulfur distribution with a higher COS concentration than one may expect. The conversion of COS to H_2S occurs mainly by COS hydrolysis, which is very slow at low temperatures. Finite rate studies indicate that an effective catalytic COS hydrolysis rate constant of 10^{-17} to 10^{-16} cm^3/mol sec will allow the reaction to reach >95% equilibrium in small enough residence time to allow reasonable reaction vessel sizes.

It is found that the achievable H_2S/COS equilibrium ratio is determined from the product of the locally frozen H_2O/CO_2 ratio and the COS hydrolysis equilibrium constant. The governing parameters for the H_2O/CO_2 equilibrium ratios are the temperature, pressure, and the gas stream (H/C) and (O/C) ratios. The higher the (H/C) ratio and the lower the (O/C) ratio the larger the H_2O/CO_2 ratio and thus the larger the H_2S/COS ratio. Moreover, raising the (H/C) ratio and lowering the (O/C) ratio also increases the achievable CH_4 equilibrium concentration from a catalytic methanation module.

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COS-H_2S RELATIONSHIPS IN PROCESSES PRODUCING LOW/MEDIUM-BTU GAS

I. INTRODUCTION

The production of gaseous and liquid fuels from domestic coal has a high priority in the overall U.S. energy policy. Of the technologies used to produce these fuels from coal, gasification and indirect liquefaction are commercially available, and therefore, will be the first generation plants constructed in the U.S.

One of the largest process and environmental concerns associated with gasification and indirect liquefaction technologies is the removal and ultimate fate of sulfur compounds formed during the gasification of coal. Sulfur compounds will poison downstream methanation and synthesis catalysts and will present a potential environmental and health problem if emitted to the atmosphere at certain levels.

The two primary sulfur compounds formed during coal gasification are H_2S and COS. Of these, the amount of COS in relation to H_2S is of primary concern because of the following reasons:

- Gaseous sulfur compounds are usually removed by an acid gas removal (AGR) process (i.e., Rectisol, Selexol, etc.). COS is less soluble than H_2S in physical AGR solvents; therefore, more energy is required to remove COS from the product gas stream to levels required for downstream processes (i.e., <5 ppm reduced sulfur).
- Because of the relative solubility, when a selective AGR operation is used, COS will distribute itself differently than H_2S in the AGR tail gases.
- Certain sulfur recovery processes (e.g., Stretford) will not remove COS from AGR tail gases and more expensive sulfur recovery processes may be required to reduce sulfur emissions from the plant.

Based on the above reasons, COS can be removed from gas streams; however, it is more difficult to remove than H_2S. In order to design AGR and sulfur recovery systems it is important to identify and understand the effect of the parameters which control the distribution of sulfur between H_2S and COS in gasifier technologies.

The conversion of COS to H_2S is limited by the hydrolysis reaction,

$$COS + H_2O \rightleftharpoons H_2S + CO_2 \quad . \qquad (I)$$

This reaction is sufficiently slow that equilibrium levels cannot be achieved. However, catalysts exist[2-4] which increase the rate of (I) and test modules are being prepared. The scope of the present study is to investigate the relationship of H_2S and COS in various gasifier technologies. Comparisons between model computations and actual gasifier measurements lends an understanding of the systematics to aid in future designs. Both equilibrium and finite rate considerations are included.

The data base[5-11] used for comparison is characterized in Table 1. As can be seen the gasifiers represent a wide diversity in gasifier technology, coal classification, and operating conditions. Table 2 shows the measured concentrations of the major species as well as the H_2S and COS levels contained in the raw product gas stream. These are the values to be used in comparisons with model calculations.

II EQUILIBRIUM COMPUTATIONS

The equilibrium concentration of molecular species at a given temperature and pressure may be calculated by minimizing Gibbs Free Energy constrained by the conservation of mass for each element. We have performed such calculations for each gasification system using as input the amounts of total carbon, hydrogen, oxygen, nitrogen, and sulfur present from the measurements of the product gas streams. The data base consists of the Gibb's Free Energy of over 70 molecular species from the JANAF handbook.[12,13]

Figures 1 and 2 show typical results from such calculations. Figure 1 corresponds to the CO_2 Acceptor[9] and Figure 2 to the Wilputte-Chapman[8]. The bars on each plot show the measured levels (with 10% uncertainty) of each of the species. Figure 1 illustrates that the CO_2 Acceptor is able to maintain its equilibrium as the gas cools to about 1000K where the reactions become frozen. Although the Wilputte-Chapman results show a similar effect, the agreement is not as definitive. The CO, H_2, and CH_4 are in equilibrium corresponding to approximately 900K while the H_2O is not in the same temperature range. This is most likely due to an imprecise H_2O measurement. Of the H_2S and COS, the COS measurement is much higher than equilibrium would predict at any temperature. However, this difference is only a factor of 3 and for these small concentrations, the deviation is considered to be reasonable. In general, we conclude that at least the major gaseous species (H_2O, CO_2, CO, H_2, and CH_4) are frozen at equilibrium values corresponding to temperatures in the 900-1300K range.

TABLE 1. GASIFIER CHARACTERIZATIONS

Site	Type	Technology	Coal	Gas	Pressure (atm)	Flowrate (scfs)	Identifier
Glen Gery	Wellman-Galusha	Fixed-Bed (Thick)	Anthracite	Low-Btu	1	45	GG
Fort Snelling	Wellman-Galusha	Fixed-Bed (Thick)	Lignite	Low-Btu	1	30	FS
Riley Morgan	Riley Stoker	Fixed-Bed (Thin)	Lignite	Low-Btu	1	80	RS
Holston	Wilputte-Chapman	Fixed Bed (Thin)	Subbituminous	Low-Btu	1	390	WC
Rapid City	CO_2 Acceptor	Fluidized Bed	Sublignite	Med-Btu	10	20	CA
Montebello	Texaco	Entrained Bed	Subbituminous	Med-btu	24	800	T
Hanna	UCG	In-Situ	Subbituminous	Low-Btu	5	55	UCG

TABLE 2. PRODUCT STREAM COMPOSITIONS[a]

Gasifier[b]	N_2 (vol %)	H_2 (vol %)	CO (vol %)	CH_4 (vol %)	H_2O (vol %)	CO_2 (vol %)	H_2S (ppmv)	COS (ppmv)
GG	48.5	15.3	24.0	0.22	5.9	5.2	649	87
FS	37.6	12.4	21.1	0.77	19.6	7.6	892	115
RS	33.9	13.2	20.3	0.77	25.6	5.3	860	95
WC	50.9	13.2	17.9	1.4	7.0[c]	7.7	228	25
CA	6.0	40.7	11.7	8.8	24.7	7.1	1000	7.5
T	0.3	34.0	43.8	0.029	0.47[d]	21.1	1264	48
UCG	47.1	14.4	11.4	2.6	11.7	11.8	2584	84

[a] Only major species, H_2S and COS compositions given.

[b] Identifier from Table 1.

[c] Estimated from partial data.

[d] Assumed value corresponding to saturation at 100F. This value is a lower bound to the H_2O level in the gas stream. The actual value is probably much higher.

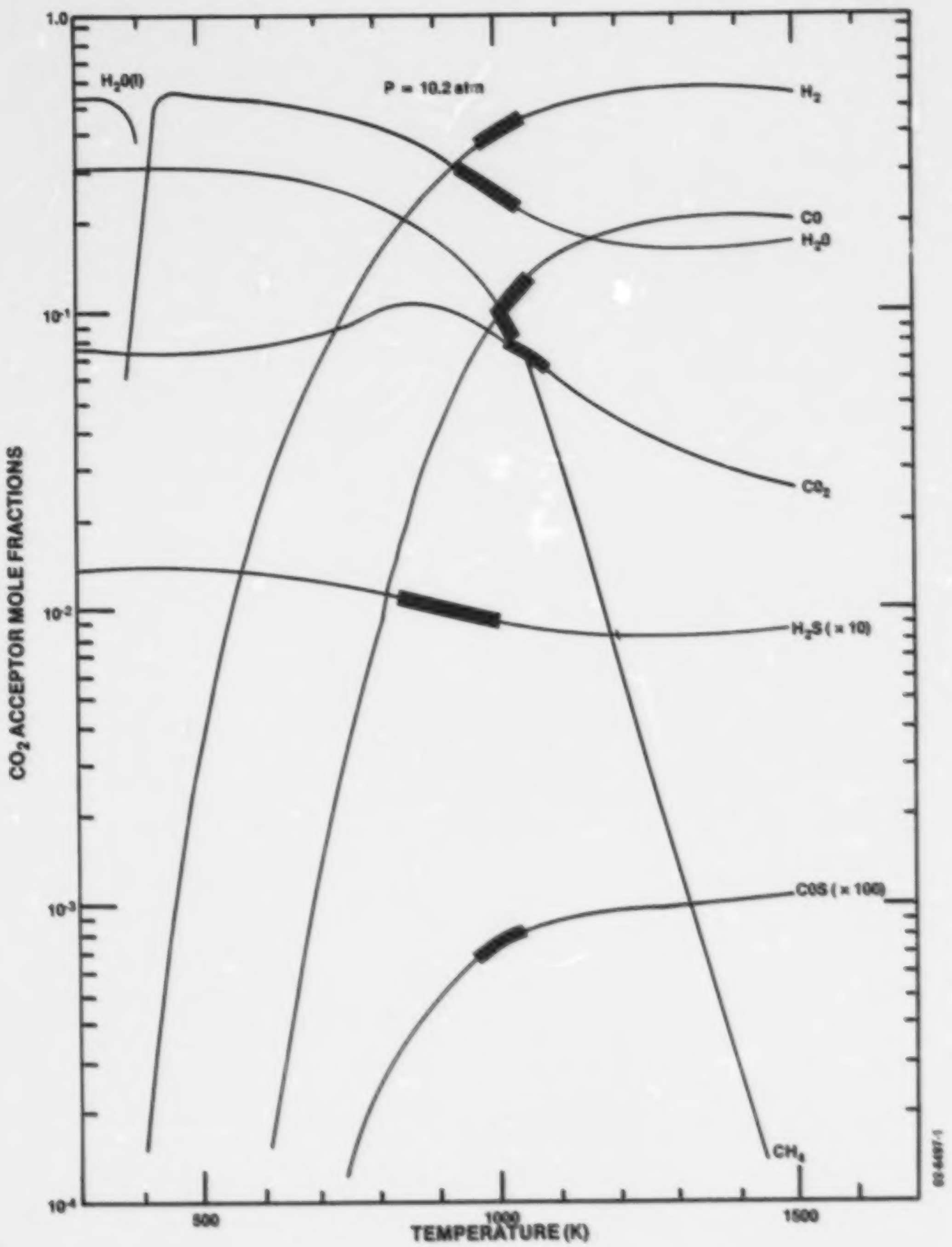

Figure 1. Plot of the Calculated Equilibrium Major Gas Species and the H_2S-COS Distributions as a Function of Temperature for the CO_2 Acceptor Gasifier. Bars indicate actual measured levels (with 10% uncertainty).

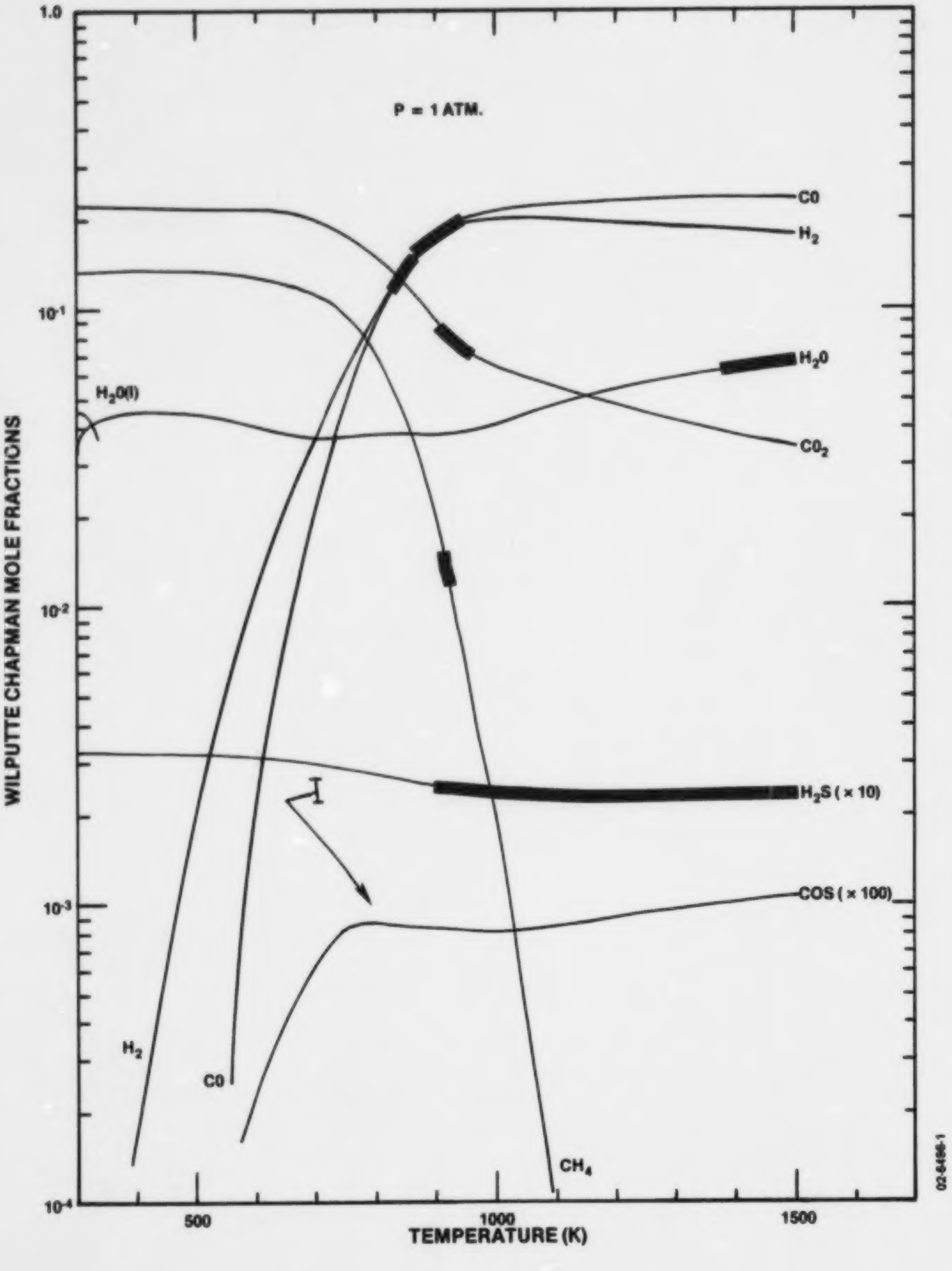

Figure 2. Plot of the Calculated Equilibrium Major Gas Species and the H_2S-COS Distributions as a Function of Temperature for the Wilputte-Chapman Gasifier. Bars indicate actual measured levels (with 10% uncertainty).

Figure 3 gives the calculated values for the H_2S/COS ratio (by volume) for each of the gasifiers as a function of temperature assuming the system maintains equilibrium at all temperatures. It should be noted that the measured H_2S/COS ratios for only the CO_2 Acceptor (CA) and the in-situ (UCG) gasifiers correspond to H_2S-COS equilibrium at any temperature; all others show actual levels much lower than their equilibrium level. This is a clear indication that if equilibrium could be achieved between H_2S and COS much more of the sulfur would be in the form of H_2S, especially at lower temperatures.

If H_2S and COS were at equilibrium then reaction I shows that the H_2S/COS ratio is directly related to the H_2O/CO_2 ratio by the equilibrium constant, K_I, namely,

$$\left(\frac{H_2S}{COS}\right) = \left(\frac{H_2O}{CO_2}\right) \quad K_I \quad . \tag{1}$$

Since K_I is monotonically increasing with decreasing temperature as shown in Figure 4, the larger the H_2O/CO_2 ratio is the larger the H_2S/COS ratio will be. Figure 5 shows the behavior of the equilibrium H_2O/CO_2 ratio with changing temperature. Again bars indicate the actual measurements. Note that the H_2O/CO_2 ratios form a family of curves related by the H/C ratio by weight. As may be expected, the higher the H/C ratio the greater the H_2O/CO_2 ratio.

Now, if a catalytic module were added to increase the rate toward equilibrium of reaction I, and since the H_2S and COS are present in very low concentrations compared to H_2O and CO_2, H_2S/COS equilibrium would be obtained without significantly affecting the H_2O and CO_2 concentrations. Here the equilibrium H_2S/COS ratios will not be as in Figure 4 but will have the form

$$\left(\frac{H_2S}{COS}\right) = \text{(constant)} \quad K_I \quad , \tag{2}$$

where the constant in Equation (2) is the frozen value of H_2O/CO_2. Figure 6 shows the possible equilibrium values achievable for the gasifiers studied here. These are simply $K_I(T)$ multiplied by the actual (H_2O/CO_2) ratio of each gasifier. The equilibrium values of $H_2S/COS \equiv R^*$ are plotted on the left hand axis. If only 90% of equilibrium were reached, i.e., $H_2S/COS = 0.9R^*$, then the fraction of sulfur as H_2S is $H_2S/(H_2S + COS) = 0.9R^*/(0.9R^* + 1)$. The right hand axis is scaled to this fraction. Therefore, if the module achieved 90% equilibrium at 500K nearly all gasifiers would yield >99.9% of all sulfur as H_2S.

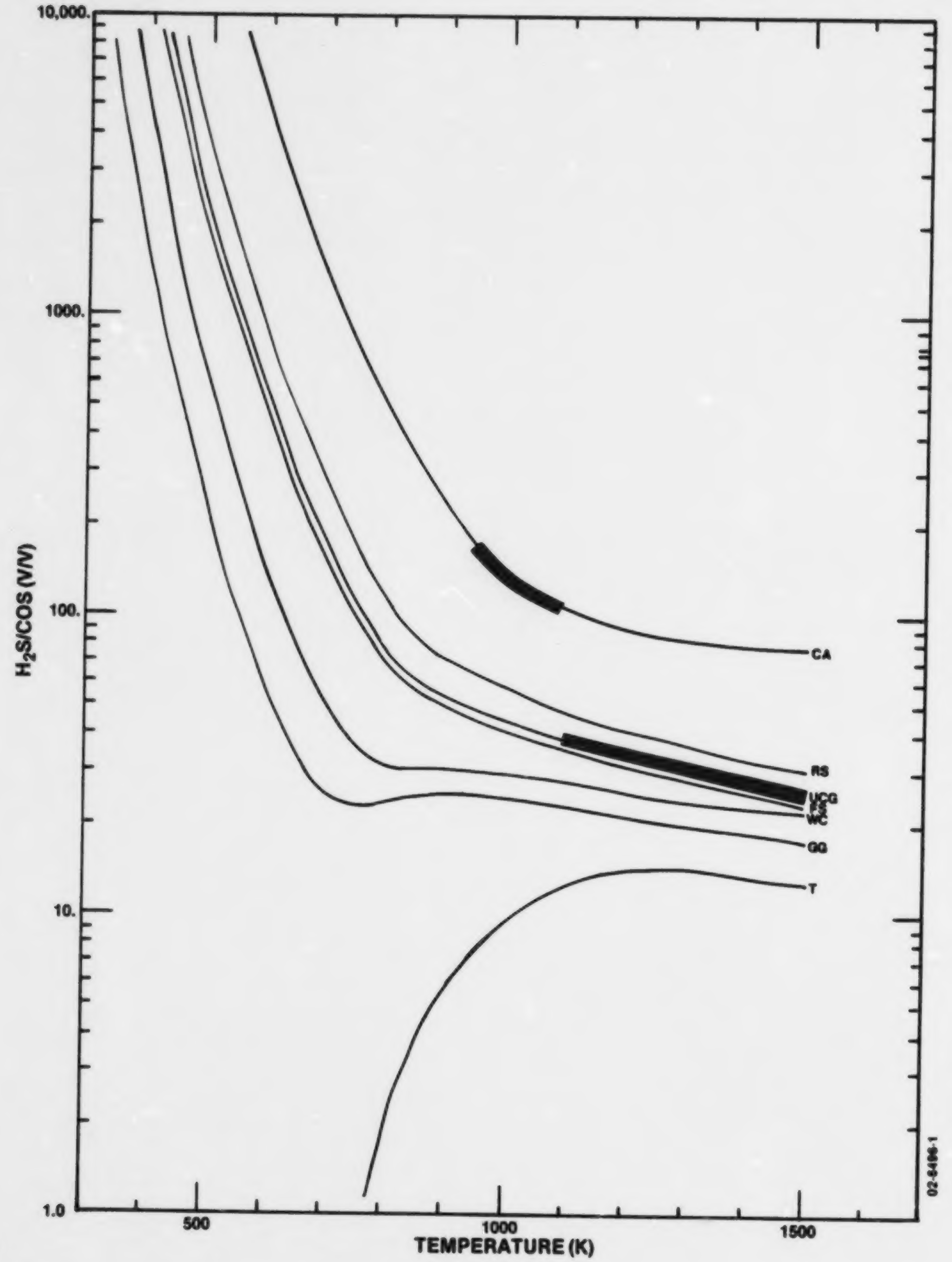

Figure 3. Plot of the Calculated H_2S-COS (by volume) Ratio Corresponding to Total System Equilibrium for Each Gasifier. Identifiers are as in Table 1. Bars indicate actual measured levels (with 10% uncertainty).

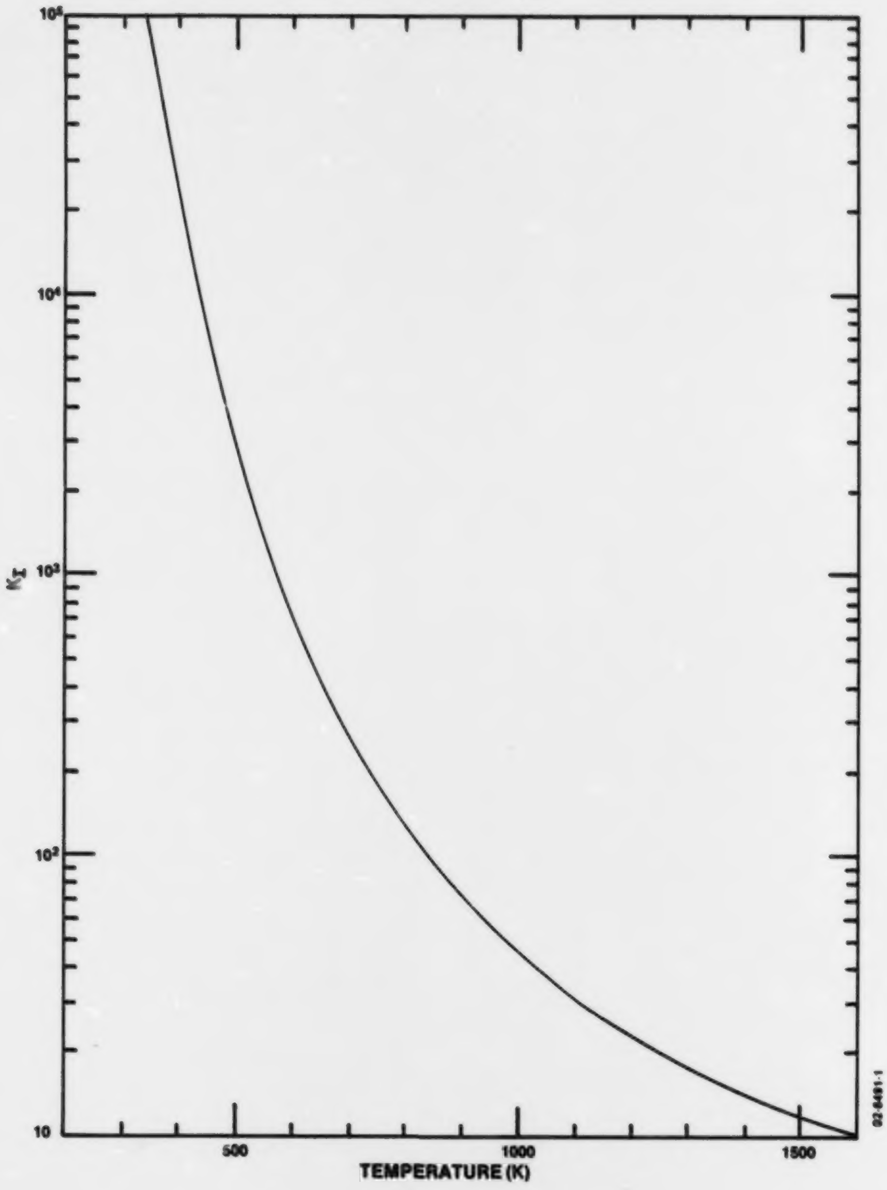

Figure 4. Plot of the COS Hydrolysis Equilibrium Constant as a Function of Temperature.

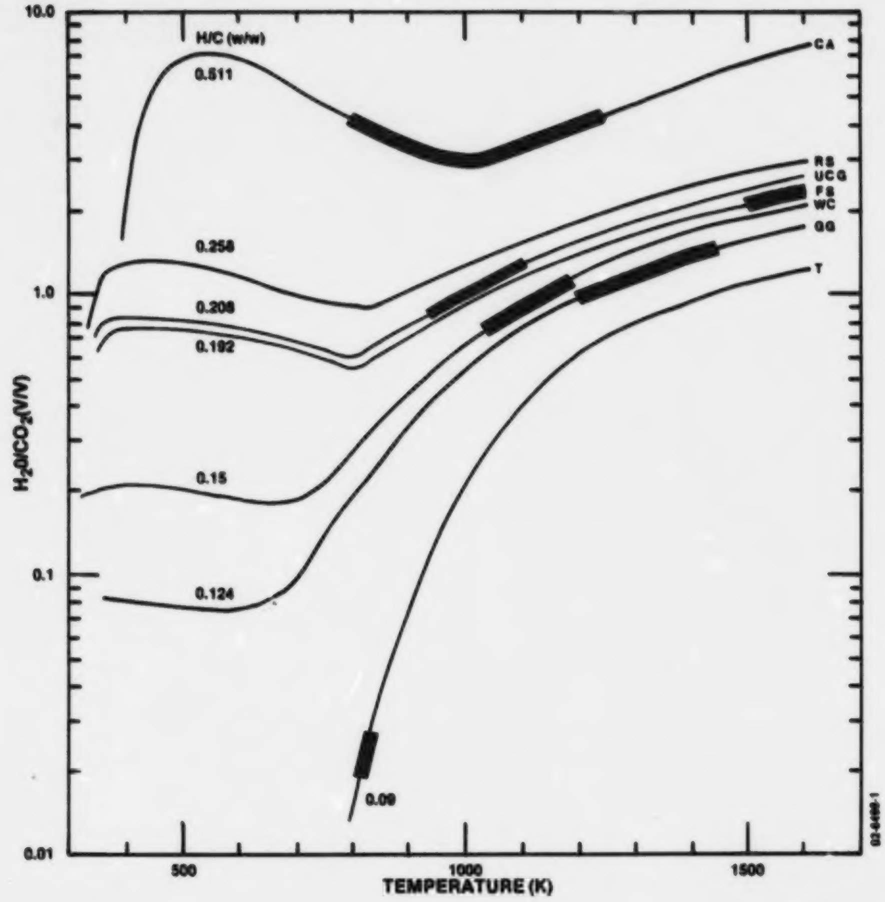

Figure 5. Plot of the Calculated H_2O/CO_2 (by volume) Equilibrium Ratio for Each of the Gasifiers. Identifiers are as in Table 1. Bars indicate actual measured levels (with 10% uncertainty).

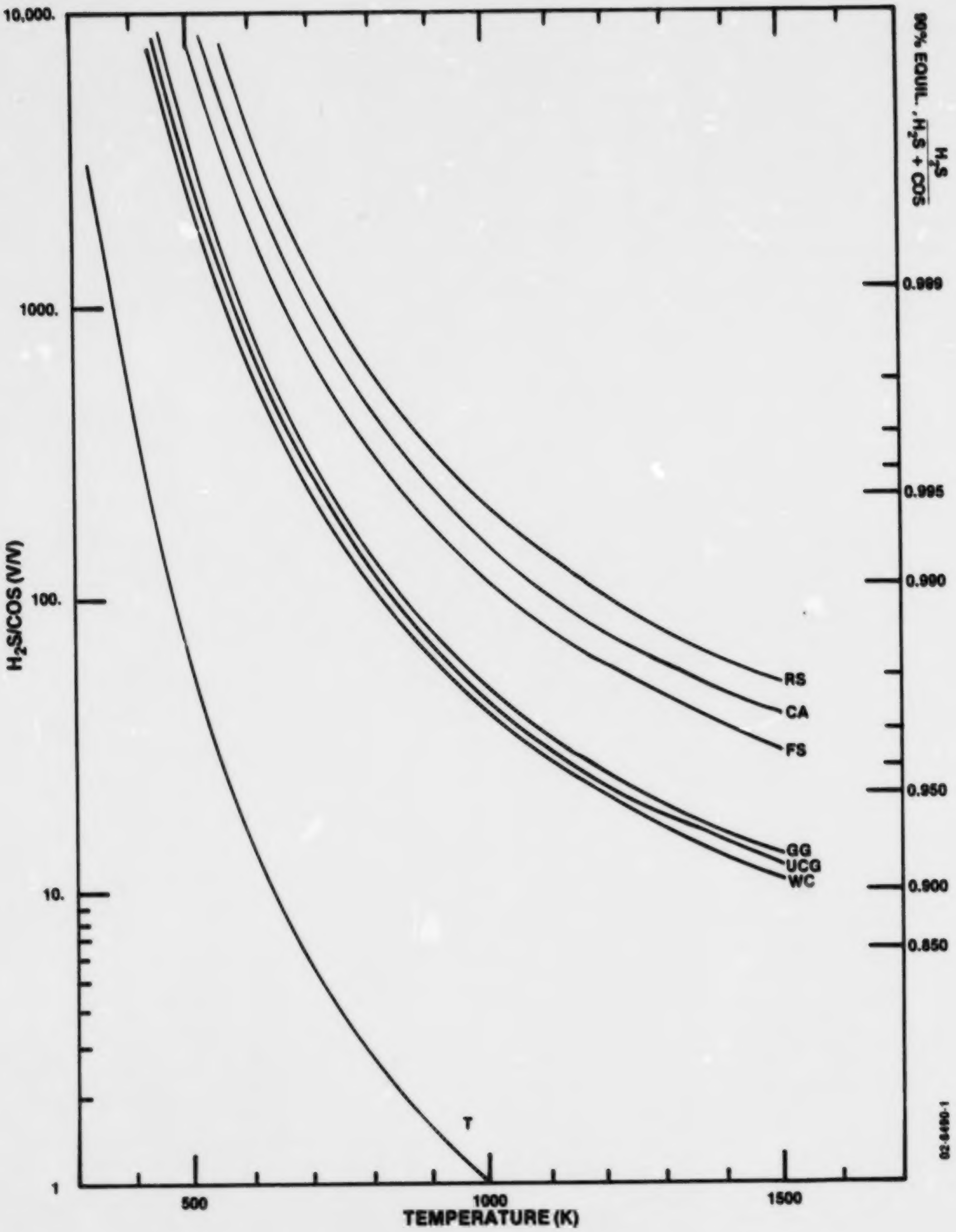

Figure 6. Plot of the Achievable H_2S/COS (by volume) ratio for Each of the Gasifiers Assuming a Frozen H_2O/CO_2 Ratio Corresponding to Measured Levels and COS Hydrolysis Equilibrium. Identifiers are as in Table 1.

It is clear that the greater the H_2O/CO_2 ratio the greater the achievable H_2S/COS ratio. Therefore, it is worth considering which parameters determine the H_2O/CO_2 ratio. Both H_2O and CO_2 are major species in the gas phase and as such they will only be affected by the other major species. Of the major elements present (C, H, O, and N) only the C, H, and O will affect the H_2O/CO_2 ratio. Moreover, since we are only interested in a ratio, only the (total H/total C) and (total O/total C) ratios in the gas stream are important to the equilibrium. Figure 7 shows the correlation of the gasifiers between the O/C and H/C ratios by weight, designated $(O/C)_w$ and $(H/C)_w$, respectively. The $(O/C)_w$ ratio for each gasifier (except the CO_2 Acceptor) is empirically related to the $(H/C)_w$ ratio by

$$(O/C)_w = 7.6\ (H/C)_w + 0.88 \quad . \qquad (3)$$

The $(O/C)_w$ ratio is much lower in the CO_2 Acceptor due to the removal of CO_2 to form $CaCO_3$ in the fluidized bed, and the absence of O_2 in the input stream.

Using the relationship of Equation (3) the H_2O/CO_2 equilibrium ratio is uniquely determined from the $(H/C)_w$ ratio. Separate equilibrium computations were performed for atmospheric pressure considering only H, C, and O with various $(H/C)_w$ ratios and Equation (3). The result for the H_2O/CO_2 ratio are presented in Figure 8. Comparing Figure 8 to Figure 5, we find the H_2O/CO_2 equilibrium ratio to be identical when conditions are the same. Moreover, even when conditions are very different, such as the CO_2 Acceptor, the H_2O/CO_2 ratio is in agreement within approximately 25% for temperature greater than 800K. Therefore, if one knew the $(H/C)_w$ ratio and approximated the temperature at which the H_2O/CO_2 becomes frozen (in most cases 1000-1200K) the achievable H_2S/COS equilibrium ratio could be estimated from Figures 4 and 8 using Equation (2).

III. FINITE RATE CONSIDERATIONS

From the previous section, it is clear that at lower temperatures nearly all of the sulfur would exist as H_2S if equilibrium for reaction I could be obtained. If a catalyst is used, the equilibrium is unaltered, only the rate at which the equilibrium is attained is increased. Several catalysts have been partially investigated[2-4] which enhance the hydrolysis of COS; however, rates are ill-defined and catalytic poisoning has not beeen well characterized. Nevertheless, it is useful to understand the effect of various rate constants on the design of catalytic COS hydrolysis process modules.

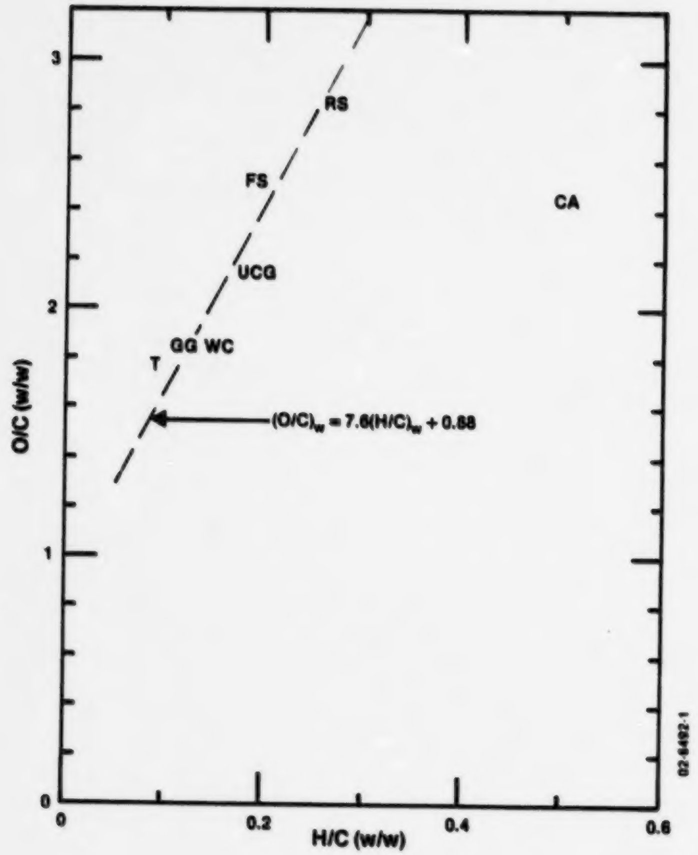

Figure 7. Plot of the Gas Stream $(O/C)_w$ to $(H/C)_w$ Correlation for Each of the Gasifiers. Identifiers are as in Table 1.

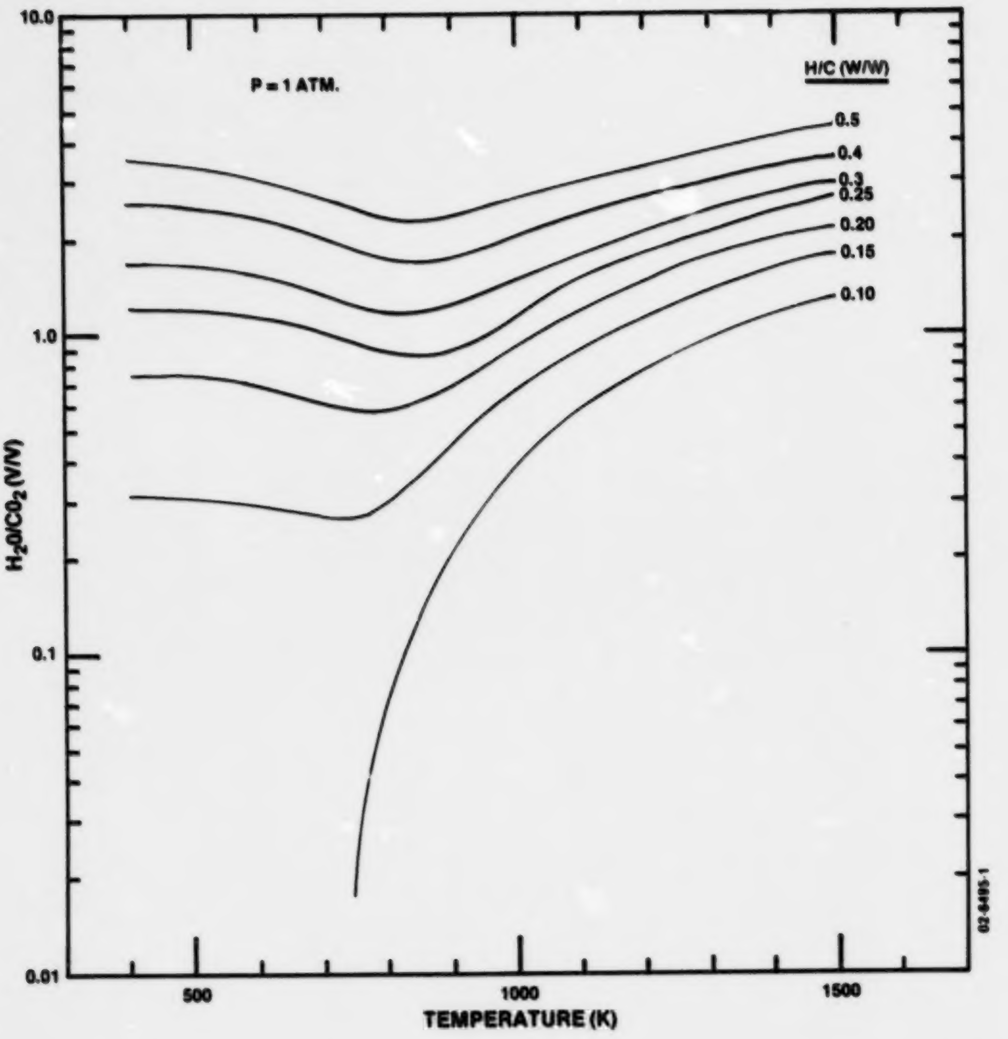

Figure 8. Plot of the Calculated Equilibrium H_2O/CO_2 Ratio as a Function of Temperature and at 1 atm. for Several $(H/C)_w$ Ratios. $(O/C)_w$ Ratios determined from Equation (3).

Consider k_f and k_r as the effective forward and reverse rate constants for Reaction I, respectively. Then the rate of change of COS is given by

$$\frac{dn_{COS}}{dt} = - k_f \, n_{H_2O} \, n_{COS} + k_r \, n_{CO_2} \, n_{H_2S} \quad . \tag{4}$$

where n_i is the density of the ith species in moles/cm^3. Now, by conservation of sulfur species

$$n_{total,S} = n^{\circ}_{COS} + n^{\circ}_{H_2S} = n_{COS} + n_{H_2S} = n^{*}_{COS} + n^{*}_{H_2S} \quad . \tag{5}$$

where the superscript "o" and asterick indicate, respectively, the initial and equilibrium values. Using Equation (5) in Equation (4) and recognizing that $K_I = k_f/k_r$, Equation (4) may be rewritten

$$\frac{dn_{COS}}{dt} = - \alpha \, n_{COS} + \beta \quad , \tag{6a}$$

where

$$\alpha = k_f \, n_{H_2O} \left(1 + \frac{n_{CO_2}}{K_I \, n_{H_2O}}\right) \quad , \tag{6b}$$

and

$$\beta = k_r \left(n^{\circ}_{H_2S} + n^{\circ}_{COS}\right) n_{CO_2} \tag{6c}$$

As discussed in Section II, H_2O and CO_2 are major species and remain unchanged by any redistribution of sulfur species, e.g., reaction I. Therefore, the H_2O/CO_2 ratio will be constant during the approach to the H_2S-COS equilibrium. Using this, α is time independent and may be written as

$$\alpha = k_f \, n_{H_2O} \left(1 + \frac{1}{R^*}\right) \tag{6b'}$$

where R^* is the equilibrium ratio, $n^{*}_{H_2S}/n^{*}_{COS} \equiv H_2S^*/COS^*$. Finally, the solution to Equation (6a) is given by

$$n_{COS} - n^{*}_{COS} = \left(n^{\circ}_{COS} - n^{*}_{COS}\right) e^{-\alpha t} \tag{7}$$

with α given by Equation (6b').

Defining an extent of equilibrium, γ, by

$$\gamma \equiv \frac{R}{R^*} = \frac{n_{H_2S}/n_{COS}}{n^*_{H_2S}/n^*_{COS}} , \tag{8}$$

and after considerable manipulation, we find

$$\gamma = \frac{\gamma_0 + R^* - R^* (1 - \gamma_0)e^{-\alpha t}}{\gamma_0 + R^* + (1 - \gamma_0)e^{-\alpha t}} , \tag{9}$$

where γ_0 corresponds to the initial value of γ.

Toward obtaining residence times to reach a given extent of equilibrium, Equation (9) may be rearranged as

$$\alpha t = \ln \frac{(\gamma + R^*)\ (1 - \gamma_0)}{(\gamma_0 + R^*)\ (1 - \gamma)} . \tag{10}$$

Now using the ideal gas relationship for the total gas phase density (n), and $n_{H_2O} = X_{H_2O} n$, where X_{H_2O} is the H_2O mole fraction, α [cf. Equation (6b')] is given by

$$\alpha = 7.34 \times 10^{21}\ X_{H_2O}\ k_f \left(\frac{P}{T}\right) (1 + \frac{1}{R^*}) , \tag{11}$$

where P and T are the pressure and temperature, respectively. Substituting Equation (11) into Equation (10), we find

$$X_{H_2O}\ k_f\ P\tau/T = 1.36 \times 10^{-22}\ \frac{R^*}{1 + R^*}\ \ln \frac{(\gamma + R^*)(1 - \gamma_0)}{(\gamma_0 + R^*)(1 - \gamma)} \tag{12}$$

If $t = \tau$ is the time to reach 90% of equilibrium then $\gamma = 0.9$ and the right hand side is a given value depending on the achievable equilibrium ratio R* and the initial value γ_0.

Table 3 presents these values for a wide range of γ_0 and R* for $\gamma = 0.85, 0.90, 0.95$. As can be seen, the entries are relatively independent of γ_0 and R*, and all entries are well represented by

$$X_{H_2O}\, k_f\, P\tau/T = \begin{cases} 1.5 \pm 1 \times 10^{-22} & \gamma = 0.85 \\ 2.0 \pm 1 \times 10^{-22} & \gamma = 0.90 \\ 3.0 \pm 1 \times 10^{-22} & \gamma = 0.95 \end{cases} \quad . \tag{13}$$

In fact, all three categories may be summarized by

$$X_{H_2O}\, k_f\, P\tau/T = 2.0 \pm 2 \times 10^{-22} \tag{14}$$

or, for a given process with a given rate constant, the reaction time necessary to achieve >95% of equilibrium is

$$\tau_R \geq 4 \times 10^{-22}\, T/X_{H_2O}\, P\, k_f \quad . \tag{15}$$

Here, we have used the conservative upper limit for the constant. The fact that these constants are all very similar in magnitude is just a reflection of the nature of first order kinetics. That is, these constants represent the driving force toward equilibrium and the further the system is from equilibrium initially, the faster the approach to equilibrium, providing similar times to reach the desired extent of reaction. Now, the required residence time in a reactor (reaction time) is related to the reactor volume, V, and the actual gas flowrate, F, by

$$\tau_R = V/F = 300\, V\, P/F_o\, T \quad , \tag{16}$$

where F_o is the flowrate at 300K and 1 atm. Therefore, Equation (15) may be rewritten

$$\frac{V}{F_o} \geq 1.33 \times 10^{-24}\, T^2/X_{H_2O}\, P^2\, k_f \quad . \tag{17}$$

TABLE 3. EQUILIBRIUM DRIVING FORCES[a]

$\gamma_0 \backslash R^*$	10^0	10^1	10^2	10^3	10^4
			$\gamma = 0.85$		
10^{-4}	1.71	2.45	2.57	2.58	2.58
10^{-3}	1.71	2.45	2.56	2.58	2.58
10^{-2}	1.69	2.43	2.55	2.56	2.56
10^{-1}	1.57	2.30	2.42	2.44	2.44
0.5	0.96	1.53	1.63	1.64	1.64
0.7	0.53	0.87	0.94	0.94	0.94
			$\gamma = 0.90$		
10^{-4}	2.00	2.95	3.11	3.13	3.13
10^{-3}	2.00	2.95	3.11	3.13	3.13
10^{-2}	1.99	2.94	3.10	3.12	3.12
10^{-1}	1.87	2.81	2.97	2.99	2.99
0.5	1.26	2.04	2.17	2.19	2.19
0.7	0.82	1.38	1.48	1.49	1.49
			$\gamma = 0.95$		
10^{-4}	2.49	3.82	4.05	4.07	4.07
10^{-3}	2.49	3.81	4.05	4.07	4.07
10^{-2}	2.48	3.80	4.03	4.06	4.06
10^{-1}	2.35	3.67	3.90	3.93	3.93
0.5	1.74	2.90	3.11	3.13	3.13
0.7	1.31	2.24	2.42	2.43	2.43

[a] Entries correspond to $10^{22}\ X_{H_2O}\ k_f P\tau/T$.

Equation (17) may be thought of as a design criterion for a process module. It relates the necessary volume of the module to the governing parameters, Figure 9 shows a log-log plot of V/F_o vs k_f for each of the gasifier conditions with a process module temperature of 500K. V/F_o values above the line correspond to a sufficiently sized process module for a given effective rate constant to achieve 95% equilibrium. The two horizontal dashed lines correspond to large scale systems (flowrates of 3000 SCF/sec) with modules of 1000 and 100 ft^3. For these parameters, the catalytic rate must be $k_f \sim 10^{-17}$-10^{-16} cm^3/mol-sec to handle all gasifiers. The noncatalytic gas phase rate constant is not known but is estimated to be 10^{-26}-10^{-24} cm^3/molsec at 500K. This would correspond to an activation energy of approximately 15000K. Since catalytic enhancement is thought to reduce the activation energy to approximately 3000K, this type of catalytic module would appear encouraging.

IV. EQUILIBRIUM REVISITED

In the previous section the governing parameters and their relationship to the process module were determined. With them, once the effective hydrolysis rate constant is determined, an optimal module may be designed. This model presents the parameters necessary to reach a desired fraction of the equilibrium H_2S/COS ratio. This ratio is determined by the gasifier operating conditions. As noted earlier, the H_2S/COS equilibrium ratio is directly related to the COS hydrolysis equilibrium constant by the frozen H_2O/CO_2 ratio in the gas stream. Since the value of the H_2S/COS ratio is so important to the attainable sulfur redistribution in the process module, a few points should be noted regarding this ratio and any effect on the gaseous product fuel.

Although the minimization of Gibbs Free Energy is a numerically efficient and general method of obtaining the equilibrium compositions, often the more explicit method of solving equilibrium constant expressions can lead to insights obscured by the above technique. In a gasifier, the major molecular participants are H_2, CO, CH_4, H_2O, and CO_2. Therefore, there are only five conditions necessary to determine the concentrations of these species. These are the three elemental conservation equations and two additional chemical equilibrium equations. Namely

$$H = 2H_2 + 2H_2O + 4CH_4 \qquad \text{II}$$
$$O = H_2O + CO + 2CO_2 \qquad \text{III}$$
$$C = CO + CO_2 + CH_4 \qquad \text{IV}$$
$$H_2O + CO = CO_2 + H_2 \qquad \text{V}$$
$$3H_2 + CO = H_2O + CH_4 \qquad \text{VI}$$

The two chemical equations are the water-gas shift (V) and methanation (VI) reactions.

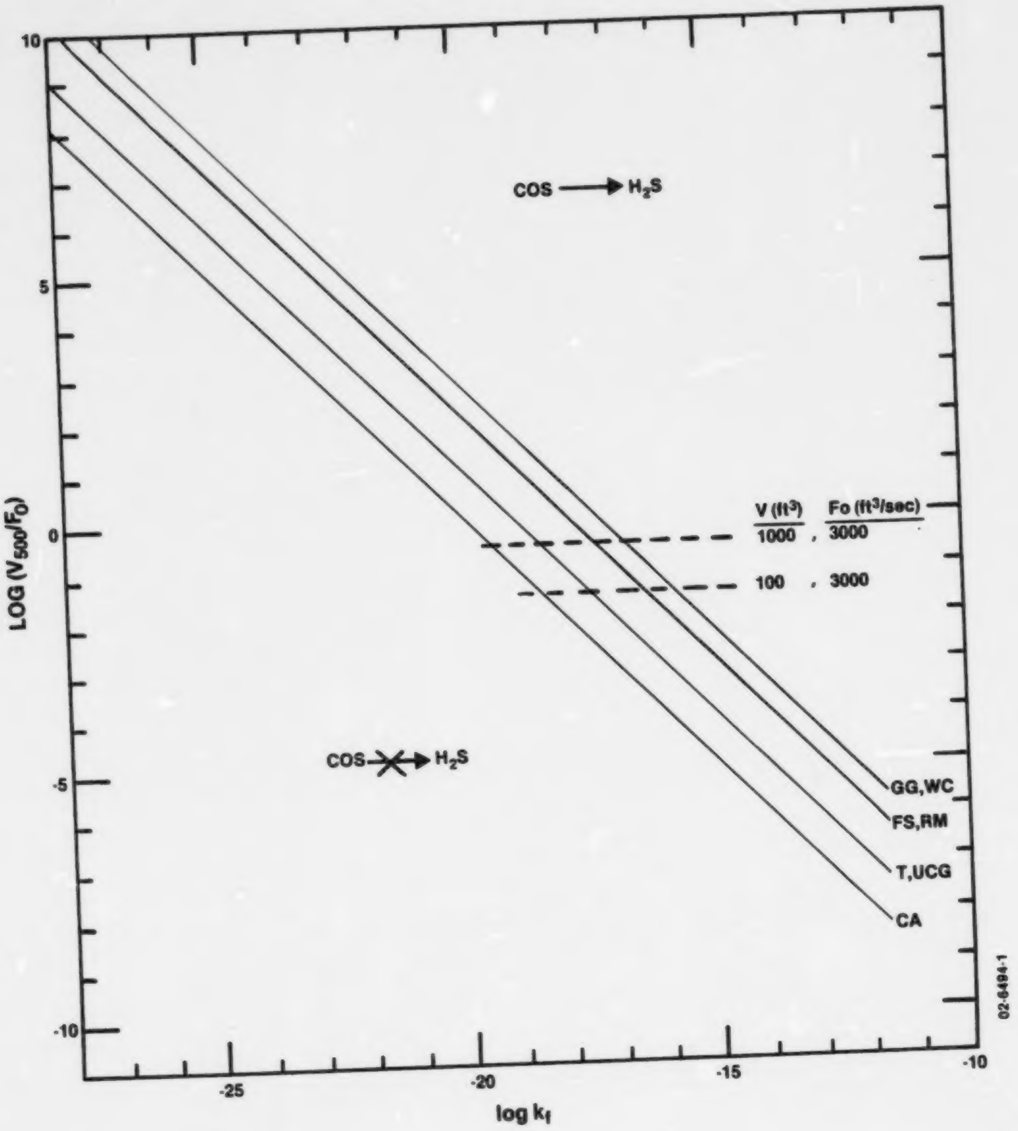

Figure 9. Log-Log Plot of V/F_o vs. k_f for Each of the Gasifiers Corresponding to a Process Module Temperature of 500K. Area above the Lines Corresponds to Conditions such that the Reaction will Achieve Equilibrium. Below the lines the ratio is too slow for the reaction to proceed.

Now, the equilibrium of the methanation reaction is such that at high temperatures the equilibrium is totally shifted to the left, with no CH_4 present. At lower temperatures, equilibrium is with the CH_4 formation, however, rates became too slow to achieve the equilibrium. Since CH_4 is a more economical fuel, often a methanation module is added to convert the H_2 and CO to CH_4. Therefore, it is important to understand the equilibrium over the entire range of temperatures.

The equilibrium is naturally divided into three temperature regions denoted by A, B, and C. Only in region B are all five molecular species present. The molecular distribution of major species within the regions are:

A: CH_4, H_2O, CO_2 ($T \lesssim 700K$)

B: CH_4, H_2O, CO_2, H_2, CO ($700 \lesssim T \lesssim 1100K$)

C: H_2O, CO_2, H_2, CO ($T \gtrsim 1100K$)

Therefore, since the molecular species are reduced in regions A and C, only B requires the entire (II-VI) set of equilibrium conditions. In regions A and C, the conditions become

region A:

$$H = 2H_2O + 4CH_4 \qquad \text{II}'$$
$$O = H_2O + 2CO_2 \qquad \text{III}'$$
$$C = CO_2 + CH_4 \qquad \text{IV}'$$

and

region C:

$$H = 2H_2 + 2H_2O \qquad \text{II}''$$
$$O = H_2O + CO + 2CO_2 \qquad \text{III}''$$
$$C = CO + CO_2 \qquad \text{IV}''$$
$$H_2O + CO = CO_2 + H_2 \qquad \text{V}$$

In region A the molecular distribution of major species is trivially determined from the conservation equations.

The solution (per mole of carbon) in region A is

$$\left(\frac{CH_4}{C}\right) = \frac{3}{2}\left(\frac{H}{C}\right)_w - \frac{3}{16}\left(\frac{O}{C}\right)_w + \frac{1}{2} \quad , \tag{18a}$$

$$\left(\frac{H_2O}{C}\right) = 3\left(\frac{H}{C}\right)_w + \frac{3}{8}\left(\frac{O}{C}\right)_w - 1 \quad , \tag{18b}$$

$$\left(\frac{CO_2}{C}\right) = \frac{1}{2} - \frac{3}{2}\left(\frac{H}{C}\right)_w + \frac{3}{16}\left(\frac{O}{C}\right)_w \quad . \tag{18c}$$

Therefore, as $(H/C)_w$ is increased, the yield of CH_4 and H_2O is increased and CO_2 is decreased, while as $(O/C)_w$ is increased the yield of CH_4 is decreased with H_2O and CO_2 being increased. Note that there is no pressure or temperature dependence within this region.

Region C has a temperature dependence due to the addition of the water gas reaction (V). However, since there is no change in the number of moles during this reaction there is no pressure dependence throughout this region. The solution for the molecular species within this region is

$$\left(\frac{H_2O}{C}\right) = \frac{3}{4}\left(\frac{O}{C}\right)_w - 1 - \left(\frac{CO_2}{C}\right) \quad , \tag{19a}$$

$$\left(\frac{CO}{C}\right) = 1 - \left(\frac{CO_2}{C}\right) \quad , \tag{19b}$$

$$\left(\frac{H_2}{C}\right) = 6\left(\frac{H}{C}\right)_w - \frac{3}{4}\left(\frac{O}{C}\right)_w + 1 + \left(\frac{CO_2}{C}\right) \quad , \tag{19c}$$

with

$$\left(\frac{CO_2}{C}\right) = G(T)\ [\ H^{\frac{1}{2}}(T) - 1\ ] \quad , \tag{19d}$$

where

$$G(T) = [\ 6\left(\frac{H}{C}\right)_w - \frac{3}{4}\,(1-K_V)\left(\frac{O}{C}\right)_w + 1\ ]/2(1-K_V) \ , \tag{19e}$$

and

$$H(T) = 1 + \frac{K_V}{(1-K_V)G^2}\left[\frac{3}{4}\left(\frac{O}{C}\right)_w - 1\right] \quad , \tag{19f}$$

Table 4 gives the values of K_V for several temperatures.

TABLE 4. EQUILIBRIUM CONSTANT FOR $H_2O + CO = CO_2 + H_2$

T (K)	$K_V = \frac{(CO_2)\ (H_2)}{(H_2O)\ (CO)}$
1600	0.3360
1500	0.3899
1400	0.4645
1300	0.5718
1200	0.7337
1100	0.9936
1000	1.445
900	2.315
800	4.246
700	9.472
600	28.44
500	138.0

As seen from Figures 1 and 2, the H_2O/CO_2 ratio is most likely to become frozen at temperatures corresponding to region C (or perhaps region B). In region C the H_2O/CO_2 ratios is given by,

$$\left(\frac{H_2O}{CO_2}\right) = \frac{\left[\frac{3}{4}\left(\frac{O}{C}\right)_w - 1\right]}{(CO_2/C)} - 1 \quad . \tag{20}$$

Here, an increase in $(H/C)_w$ [with constant $(O/C)_w$] implies an increase in H_2O at the expense of CO_2 and thus an increase in the H_2O/CO_2 equilibrium. Another useful simplifiction within this region is obtained when $K_V = 1$. This condition corresponds to a temperature of approximately 1100K. Here the H_2O/CO_2 ratio is easily found from

$$\left(\frac{H_2O}{CO_2}\right) = 6\left(\frac{H}{C}\right)_w \qquad T \simeq 1100K \quad . \tag{21}$$

Region B is the only one which requires the full set of equilibrium conditions, namely the addition of the methanation reaction. Since this reaction decreases the total number of moles, the corresponding equilibrium constant carries a factor of P^2. Therefore this is the only region which will show a pressure dependence as well as a temperature dependence.

Figure 10 shows a replotting of Figure 9 with the three temperature regions indicated by vertical dashed lines. The accuracy of Equations (18-21) is related by the plotted points within each region. The open circles correspond to Equation (18), the solid circles correspond to Equations (19 and 20), and the open squares correspond to Equation (21). This figure and the above discussion illustrate that for most temperatures and pressures in the gasification of coal, the equilibrium distribution of the major species may be predicted without the need for more elaborate computations. Examining these relationships, the governing parameters are found to be the temperature, pressure, and the $(H/C)_w$ and $(O/C)_w$ ratio. Moreover, using Equations (18-21) it is possible to obtain a set of conditions which will give a desired equilibrium distribution of the sulfur species. In the following section, we will examine the gasifier as a whole and discuss the effect of these parameters on the overall quality of the product gas.

V. CONCLUDING REMARKS

The gas phase chemistry of a gasifier has been studied with particular attention to the major species and their influence on the equilibrium distribution of sulfur between H_2S-COS and the size of the process module needed to achieve the desired extent of equilibrium. One important conclusion is that the

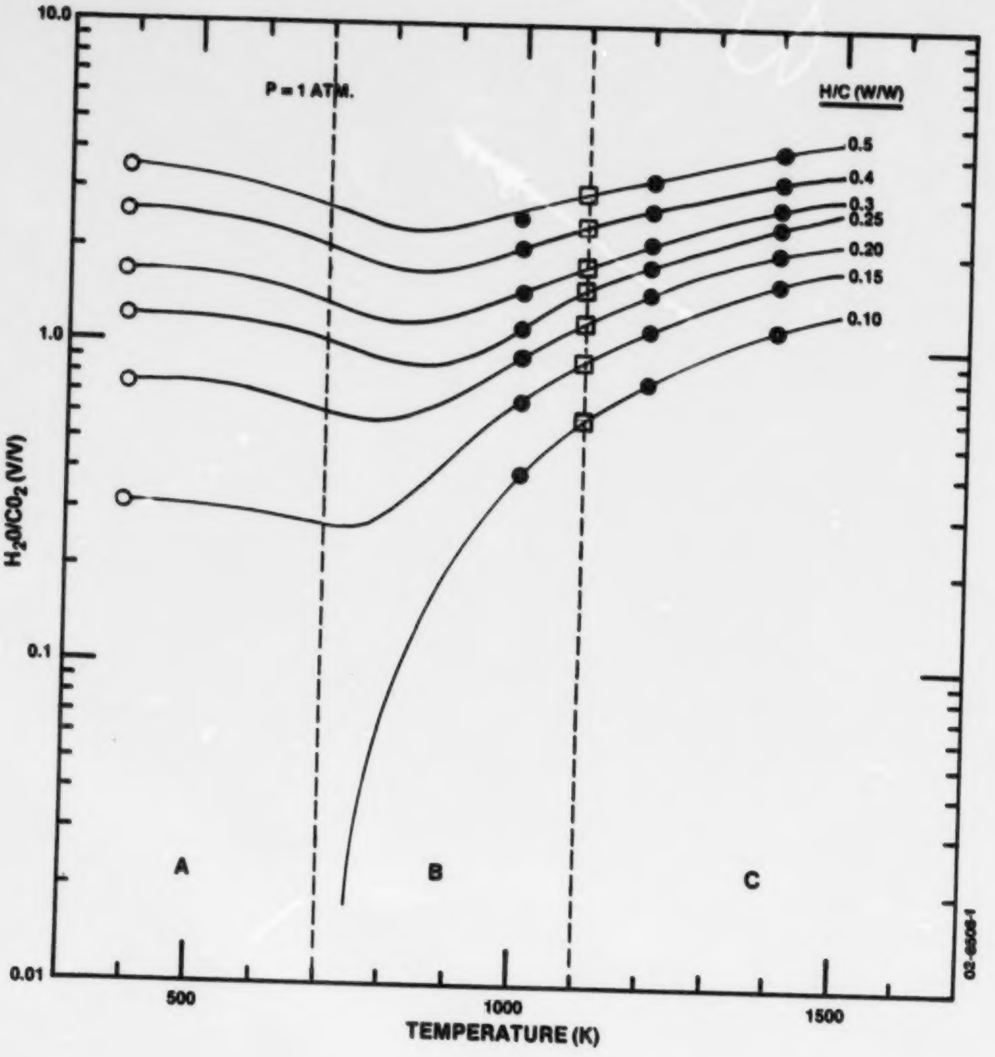

Figure 10. Plot Similar to Figure 9 Showing the Three Temperature Regions (see text). Open circles correspond to the analytical expressions of Equation (18), solid circles correspond to Equations (19 and 20), while open squares correspond to Equation (21).

residence time is essentially independent of the initial and final H_2S/COS ratios. Therefore, there are no module design criteria which depend on the desired sulfur redistribution. The attainable H_2S/COS ratio is completely determined by the local H_2O/CO_2 ratio and the COS hydrolysis equilibrium constant.

The H_2O/CO_2 ratio is controlled by the water-gas reaction at high temperatures (>1100K) and by the water-gas and methanation reactions at intermediate temperatures (700-1100K). As the gas stream is quenched upon exiting the gasifier reactor these reactions become very slow and the H_2O/CO_2 ratio becomes frozen corresponding, most likely, to its equilibrium value at the temperature of the reactor exit. Although, this temperature may be between 700 and 1100K, (i.e., the pressure dependent region), the adjoining temperature regions are pressure independent. Therefore, we expect that the H_2O/CO_2 ratio is not strongly dependent on pressure. This has been born out for the gasifiers considered in the present study.

Apart from temperature and pressure, the parameters which govern the H_2O/CO_2 equilibrium ratio are the $(H/C)_w$ and $(O/C)_w$ ratios. In general, increasing the $(H/C)_w$ and decreasing the $(O/C)_w$ ratios increases the $H_2O/-CO_2$ ratio which in turn increases the H_2S/COS equilibrium ratio. It is important to note that the affect of increasing the $(H/C)_w$ and decreasing the $(O/C)_w$ ratios also increases the equilibrium CH_4 yield. Therefore, attempting to improve the sulfur distribution not only does not lower the attainable CH_4 yield from the methanation module but actually increases it.

Although, from the above discussion, it would appear that every effort should be made to increase the $(H/C)_w$ ratio and decrease the $(O/C)_w$ ratio, this is only true within bounds. The gasification of coal requires fairly high temperatures. Moreover, the overall gasification reactions,

$$C + H_2O = CO + H_2$$
$$CO + H_2O = CO_2 + H_2$$
$$C + CO_2 = 2CO \quad ,$$

are endothermic. Thus, if heat is not continually supplied the temperature will drop and gasification will cease. This heat is produced from the combustion zone where some of the carbon is oxidized to CO_2. Now, the $(H/C)_w$ ratio may be increased by introducing more steam but this will increase the $(O/C)_w$ ratio as well. In order to decrease the $(O/C)_w$ ratio the air (or oxygen) flowrate must be decreased. However, decreasing the air will cause less combustion and therefore lower the reaction zone temperature. In actuality, increasing the steam flowrate, will increase the endothermic gasification reactions, resulting in lower temperature. Therefore, an increase in steam flowrate must be accompanyed by an increase in air (or oxygen) flowrate to maintain temperature.

In summary, the major points of this study are:

- A process module with an effective catalytic COS hydrolysis rate constant of approximately 10^{-17} to 10^{-16} $cm^3/mol\text{-}sec$ will reach >95% of the equilibrium H_2S/COS ratio in small enough residence times to allow reasonable reaction vessel sizes.
- This resonance time is essentially independent of initial and final H_2S/COS ratios.
- The achievable H_2S/COS equilibrium ratio at a given temperature is completely determined from the product of the locally frozen H_2O/CO_2 ratio and the COS hydrolysis equilibrium constant for that temperature.
- The H_2O/CO_2 ratio becomes frozen at approximately 900-1200K, probably near the reactor exit temperature.
- The governing parameters for the H_2O/CO_2 equilibrium ratios are the temperature, pressure, and the gas stream $(H/C)_w$ and $(O/C)_w$ ratios.
- The higher the $(H/C)_w$ ratio and the lower the $(O/C)_w$ ratio, the larger the H_2O/CO_2 equilibrium ratio and thus the larger the H_2S/COS equilibrium ratio.
- Raising the $(H/C)_w$ ratio and lowering the $(O/C)_w$ ratio also increases the achievable CH_4 equilibrium concentration.

ACKNOWLEDGMENTS

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BEHAVIOR OF A SEMIBATCH COAL GASIFICATION UNIT

by

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ABSTRACT

This paper describes the transient behavior of a laboratory scale fixed-bed gasifier operated in a semibatch mode. The operation is batch with respect to the coal feed and continuous with respect to gas flows. Various coals ranging from lignite to bituminous were gasified using steam-air mixtures at 1.4 MPa (200 psia) and approximately 900°C. The transient behavior of the reactor temperature at various coal bed depths was examined. Test results from nine tests involving five coals are reported. The data presented include the rate of production of various gasification products. These include CH_4, CO, H_2, benzene, toluene, xylene, H_2S, COS, and thiophene, as a function of run time. It was found that the majority of the CH_4, the minor hydrocarbons, and sulfur species were evolved during coal devolatilization. These data were analyzed using a simple kinetic model which assumes that the rate of production of a compound at any time is proportional to the (potential) amount of that compound remaining in the coal. This model explains the data reasonably well during the devolatilization period. It was found that the specific rate of production of individual species was practically the same for all coals and gasification products considered; the ultimate yield was dependent on coal type. The ultimate yield of (a) CH_4 or benzene, and (b) sulfur species roughly paralleled the volatile and sulfur contents of the coals, respectively.

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BEHAVIOR OF A SEMIBATCH COAL GASIFICATION UNIT

INTRODUCTION

The Research Triangle Institute (RTI) has performed over 40 gasification tests in a laboratory scale gasifier using a variety of coals.[1,2] During these tests, RTI has developed procedures for the sampling of the various gasifier process streams and for identifying and quantifying potential environmental pollutants found in these streams.[3]

The coal gasification tests were performed in a semibatch reactor where the experiments are batch with respect to the coal and continuous with respect to gas flows. The gasifier is approximately 6.6 cm I.D. and its 60 cm active length is surrounded by a three zone furnace. During a gasifier run, the gasifier was initially heated electrically to the desired gasification temperature of about 950°C with the desired air and steam flow passing through the gasifier. The air flows varied from 5.0 to 15.0 standard liters per minute (slpm) and steam varied from 5.0 to 18.0 slpm. After reaching gasification temperatures, the coal was batch-fed to the gasifier with the charge ranging from approximately 1.2 to 1.6 kg. The coal size was 8 x 16 mesh, and the charge was supported by a porous ceramic plate which also acted as the gas distributor.

The coal was charged to the gasifier at room temperature and, consequently, cooled the gasifier well below the initial temperature. This behavior is shown in Figure 1. Recovery of the temperature took about 30 minutes, and the rate of increase in the average bed temperature after coal drop appeared to be proportional to the difference between the average final temperature and instantaneous average bed temperature. It was found that after the recovery period, the temperature profiles in the coal bed closely matched the initial temperature profile and were dominated by the furnace except in the combustion zone of the bed.

The gasification tests were characterized by two distinct periods of operation: (1) the initial stage after the coal drop during which devolatilization of the coal occurred (surge period), and (2) a steady-state period which followed the surge and was the stage where coal gasification took place resulting in a fairly steady product gas composition.

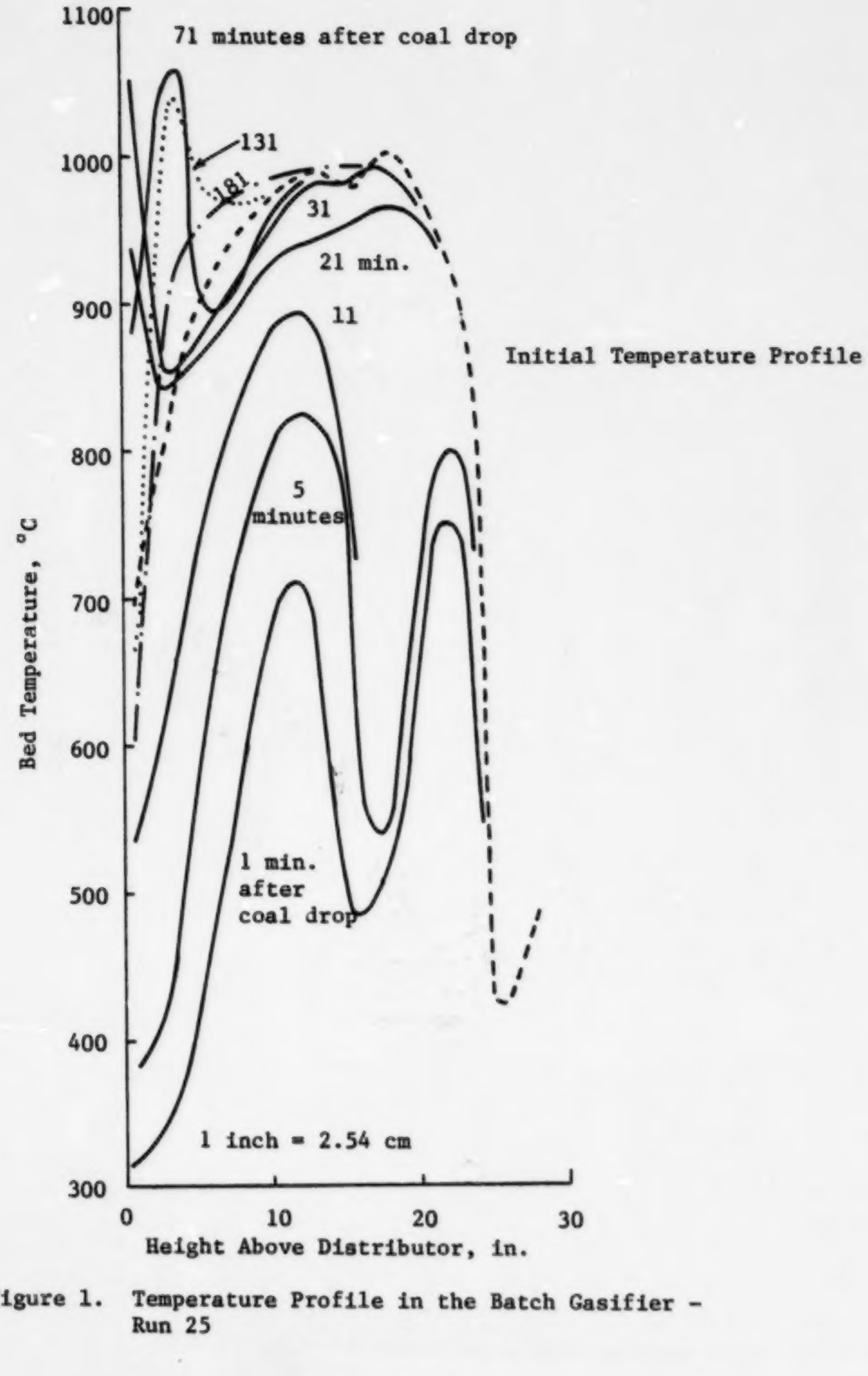

Figure 1. Temperature Profile in the Batch Gasifier - Run 25

Figures 2, 3, and 4 show the time-dependent nature of a typical gasifier test in which Illinois No.6 bituminous, Wyoming subbituminous and North Dakota lignite coals were gasified. The composition of the coals and gasification conditions are shown in Tables 1 and 2, respectively. It can be seen from these figures that production of methane and other minor hydrocarbons is greatest during the initial stage of the gasification test or during coal devolatilization. The production rate of these components fall almost two orders of magnitude from their initial rates during the surge period. A more complete description of the production rate-time characteristics of the semibatch gasification of the five coals in nine tests have been presented elsewhere.[4]

Based on the data in Figures 2, 3, and 4 and additional data presented by McMichael et al.,[4] the following observations can be made about the rate of pollutant and product production as a function of time:

1. The production of pollutants and CH_4 in the product gas usually surges to a high rate just after the coal drop, and drops quickly as the bed temperature rises. A majority of the minor components and CH_4 are formed in the first 25 to 30 minutes of the run. After this time the product rate decreases.
2. For the bituminous coals and the Montana subbituminous coal the rate of H_2 production increases during the initial stages of gasification during devolatilization. This could be a consequence of (a) increasing bed temperatures at the beginning of the run resulting in increasing H_2 formation from the steam-carbon reaction, and (b) decreased availability of reactive carbon as coal devolatilization proceeds, thus more H_2 appears in the gas. Hydrogen formation peaks early in the run, and the rate of formation decreases fairly steadily over the remainder of the run. This steady decrease is probably due to the decrease in the density of carbon in the bed with time.
3. For a steady flow of steam and air, the rate of production of CO approximately parallels the H_2 production.
4. For Illinois No.6 bituminous coal, the rate of CO_2 production reaches a maximum in the initial stage of the gasification run and then decreases or remains fairly constant. The Western Kentucky coal also shows this trend except the production rate increased sharply at oxygen breakthrough. For the subbituminous and lignite coals, CO_2 production reaches a maximum during devolatilization and then quickly drops to a minimum at about 25 minutes into the run. After this minimum the production rate increases steadily over the length of the run. The CO_2 increase is usually accompanied by a slow decrease in the rate of CO production. The reason for this could be that as the density of carbon in the bed decreases through gasification, more CO is burned in the gas phase.

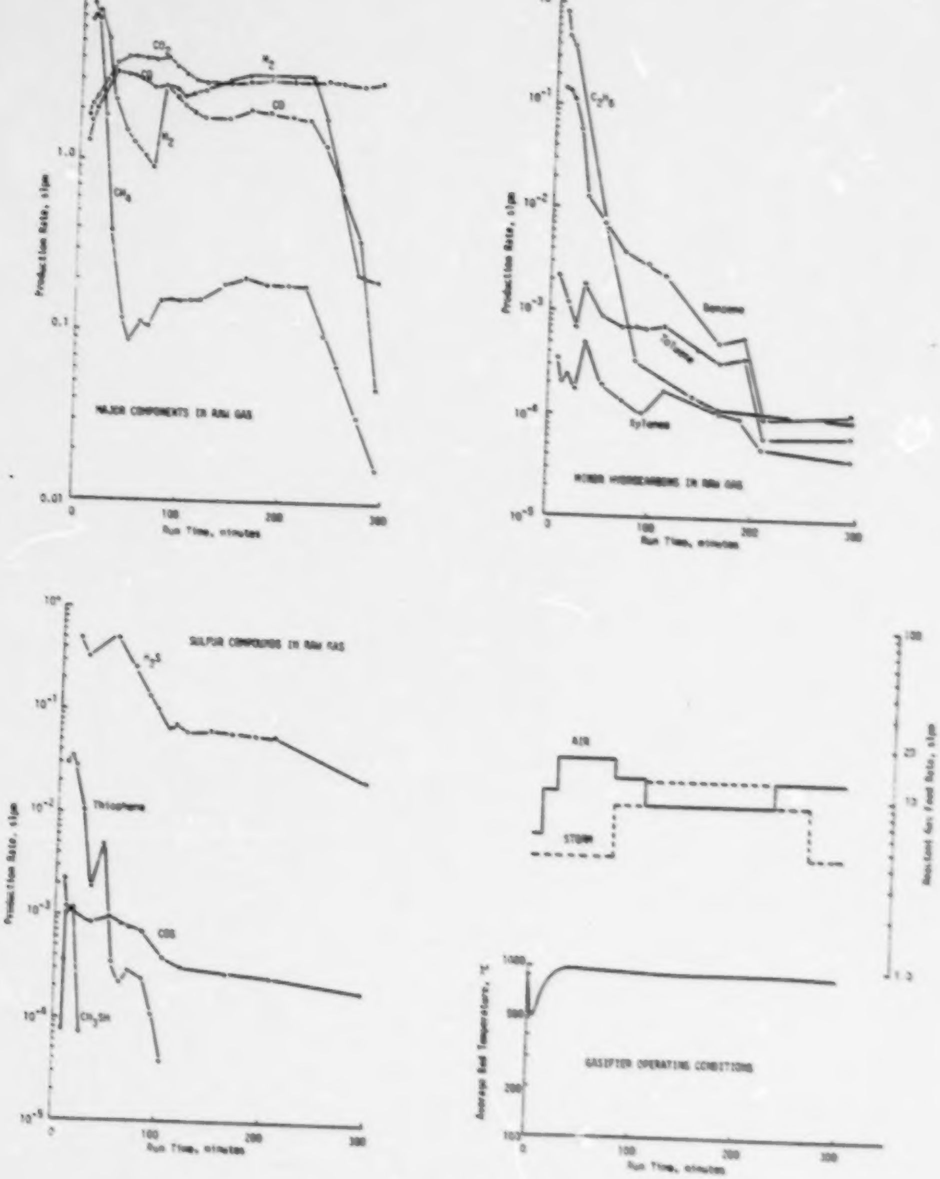

Figure 2. Gasifier operating conditions and production rate of various compounds as a function of run time - Run 23, Illinois No.6 bituminous coal.

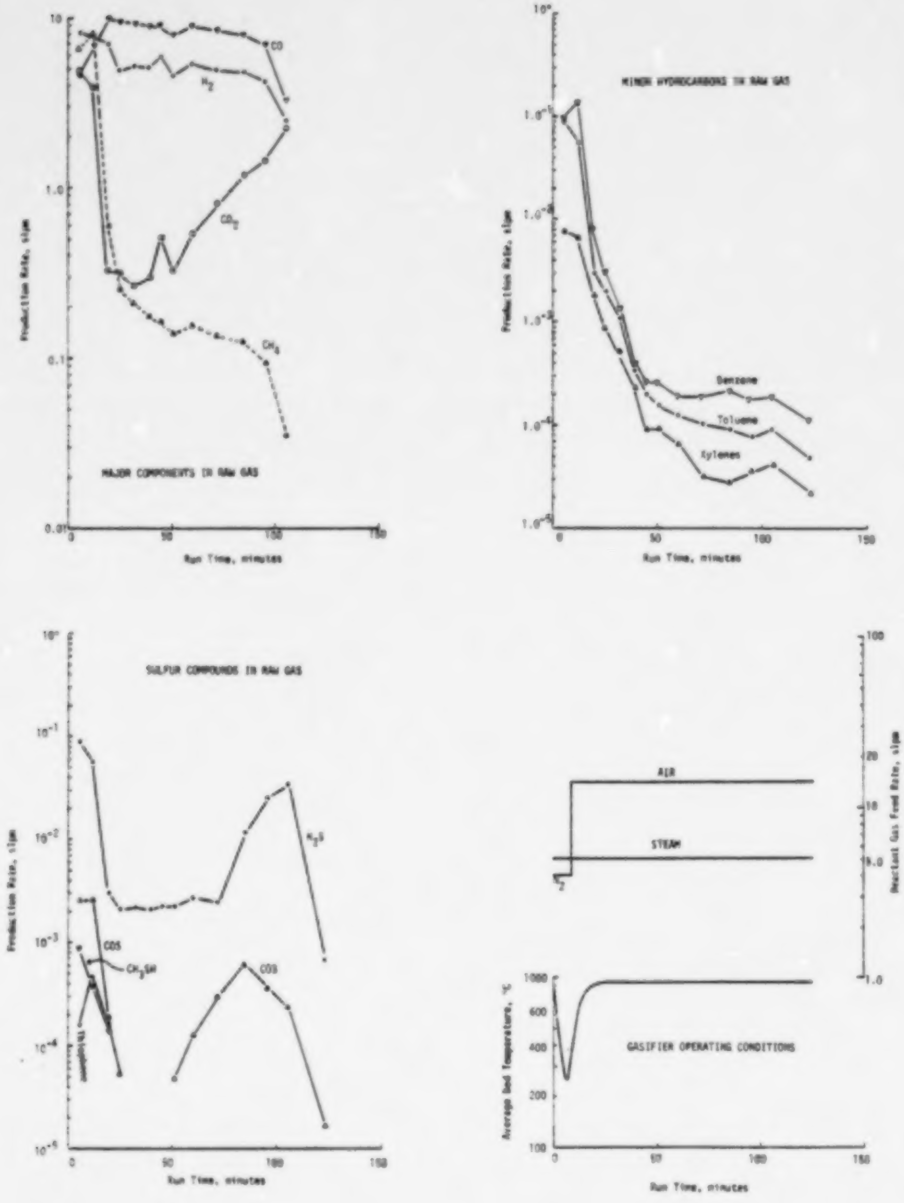

Figure 3. Gasifier operating conditions and production rate of various compounds as a function of run time - Run 33, Wyoming subbituminous coal.

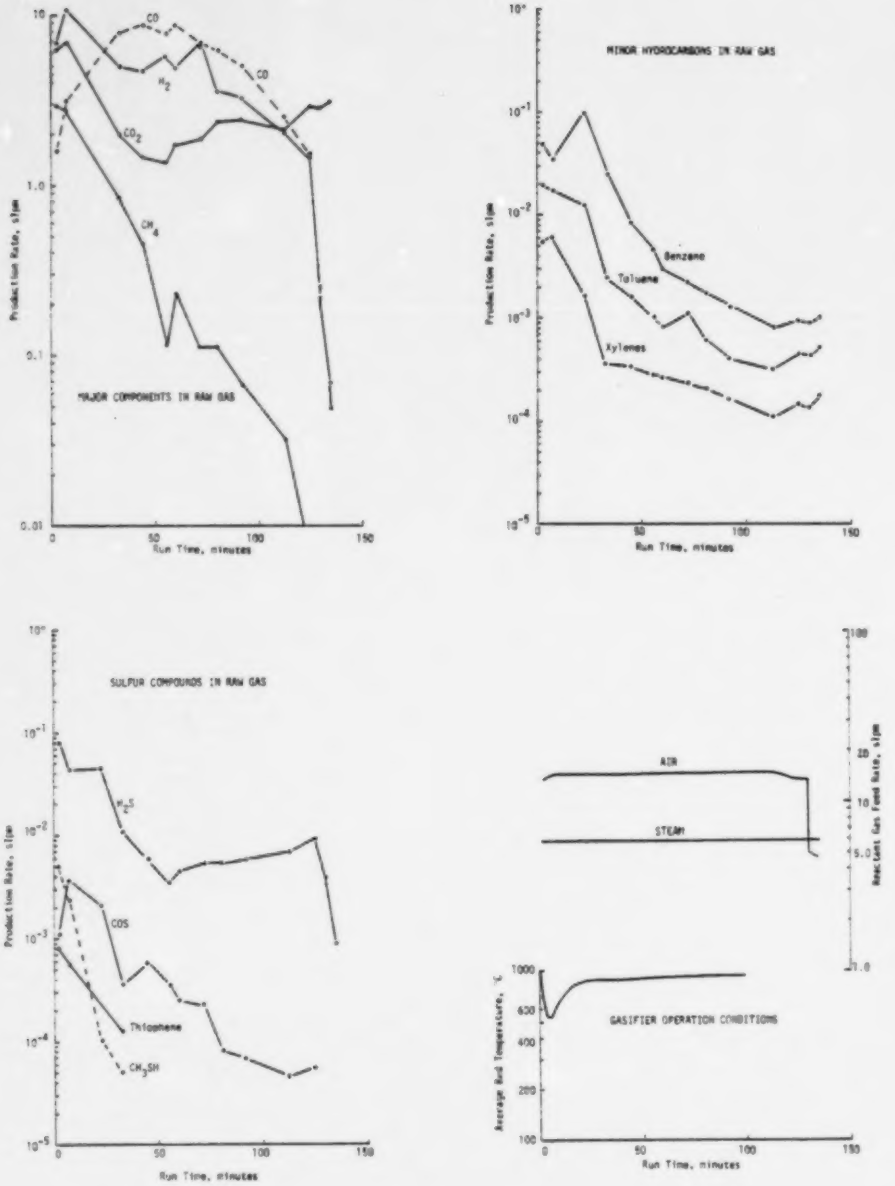

Figure 4. Gasifier operating conditions and production rate of various compounds as a function of run time - Run 36, North Dakota lignite.

TABLE 1. ANALYSIS (AS RECEIVED) OF FUELS GASIFIED

Fuel	Moisture %	Ash %	Volatile Matter %	Fixed Carbon %	Sulfate Organic Pyritic Total S	Carbon %	Hydrogen %	Oxygen %	Nitrogen %	FSI
Illinois No.6 Bituminous	5.31	11.03	34.16	49.50	0.00 1.83 1.24 3.07	66.35	5.32	12.71	1.525	3.5
Montana Rosebud Subbituminous	21.19	8.86	31.56	38.39	0.17 0.21 0.21 0.59	53.95	6.87	28.53	1.20	0.0
Wyoming Subbituminous	15.56	6.31	38.30	39.83	0.07 0.08 0.40 0.55	56.80	5.94	30.02	0.38	0.0
North Dakota Lignite	29.63	6.39	28.57	35.41	0.01 0.54 0.01 0.56	46.82	9.85	35.65	0.73	0.0
Western Kentucky No.9 Bituminous	7.03	7.83	38.78	46.36	0.05 2.69 1.70 4.44	67.36	5.58	13.71	1.08	4.0

5. The rates of production of benzene, toluene, and xylenes parallel each other. In general, benzene has the highest rate of production and the xylenes the lowest. Each has a high initial production rate. The rate decreases rapidly during devolatilization by one to two orders of magnitude.
6. The production of H_2S and COS is at a maximum during devolatilization and falls off rapidly near the end of this period. After devolatilization, H_2S and COS appear to follow the production of CO_2. This is probably due to two modes of sulfur release from the coal. The first is during devolatilization when sulfur-containing compounds are being rapidly evolved from the coal. Decomposition of these compounds results in COS and H_2S. In the second mode after devolatilization, sulfur is released by oxidation of the char matrix. Upon release the sulfur species react with H_2, CO, or CO_2 giving rise to H_2S and COS. Thus the production rate of H_2S and COS follows that of CO_2 since it is indicative of oxidation.
7. Methanethiol and thiophene are produced primarily during coal devolatilization. For each compound the production rate starts at a high initial value and falls below detection limits within 25 to 50 minutes after the coal drop.

The yield of potential environmental pollutants in the gasifier product gas over the length of the gasification runs has been computed for the RTI gasifier by integrating the rate of production with respect to time. These yields have been compared by Green, et al.[5] to yield data reported in the literature for larger scale, continuous gasifier. An example of this is shown in Table 3. It can be seen that for a majority of the components reported that the data from the RTI gasifier appears to bracket the data from the continuous gasifier even though the continuous gasifiers represent a range of gasifier operation from fixed- to fluidized-bed. Analysis of data from semibatch operation is difficult due to the unsteady nature of operation. Recently RTI has been operating its gasifier in a continuous feed mode and analysis of this data is now underway.

The initial production rates of methane and minor hydrocarbons during the devolatilization of the coal as shown in Figures 2, 3, and 4 can be interpreted in several ways. One way is in terms of the Gregory-Littlejohn equation.[6] For a constant heating rate this equation predicts a straight line on a semilog graph of rate of production of volatiles versus time. This equation could perhaps be applied to the individual components making up the total volatile yield.

TABLE 3. POLLUTANT PRODUCTION IN RAW MOISTURE-FREE PRODUCT GAS FROM GASIFICATION OF NORTH DAKOTA LIGNITE

Pollutant	Air-Blown Synthane (Mercer County) µg/g coal	CO_2 Acceptor (Velva) µg/g coal	GFETC (Velva) µg/g coal	RTI Range Beulah Zap (Mercer County) µg/g coal
Hydrogen Sulfide	9.4E3	2.1E3	1.5E3	1.7E3-2.6E3
Carbonyl Sulfide	7.6E2	9.7E1	1.3E2*	1.7E2-2.9E2
Thiophene	<3.8E1	NA	NA	3.8E0-5.7E2
Methylthiophene	<4.4E1	NA	NA	1.3E1-3.7E1
Dimethylthiophene	<5.0E1	NA	NA	1.3E0***
Methanethiol	3.4E1	NA	8.5E1**	1.3E1-7.8E1
Benzene	4.8E3	NA	NA	2.0E3-5.3E3
Toluene	5.8E2	NA	NA	1.1E3-2.1E3
Xylene	1.9E2	NA	NA	2.4E2-7.6E2
Ammonia	NA	5.5E3	NA	5.3E1-1.7E2

*Includes CS_2.
**"thiols."
***C_2-thiophenes.

Another way to interpret data of the type shown in Figures 2, 3, and 4 involves the use of a rate expression. The most commonly used kinetic approach is to assume that the rate of evolution of a volatile species is proportional to the potential amount of that species remaining in the coal.[7]

$$\frac{dV_i}{dt} = k_i \left(V_{\infty_i} - V_i \right) \qquad (1)$$

where k_i = the rate constant, min^{-1}.

V_i = the yield of the ith volatile component, sℓ/kg coal.

V_{∞_i} = the ultimate yield of the ith volatile component, sℓ/kg coal.

t = time, min.

Assuming isothermal conditions, Equation (1) can be integrated subject to $V_i = 0$ at $t = 0$ to give

$$V_\infty - V_i = V_\infty e^{-k_i t} \qquad (2)$$

Substituting Equation (2) into (1) gives

$$\frac{dV_i}{dt} = k_i V_{\infty_i} e^{-k_k t} \qquad (3)$$

Taking the log of Equation (3) yields

$$\ln \frac{dV_i}{dt} = \ln \left(k_i V_{\infty_i} \right) - k_i t \qquad (4)$$

Equation (4) predicts that a semilog plot of the rate of production of a volatile species versus time should yield a straight line with the slope equal to the negative of the rate constant and the intercept equal to the product of the ultimate yield and the rate constant. A substantial number of product rate-time curves determined in RTI's gasification experiments can be interpreted in terms of Equation (4) if the rate constant, k_i, is viewed as an average constant over the period of the linear data. This can be done if the rate constant is not a strong function of temperature such as would be the case in diffusion-controlled processes.

A kinetic analysis has been made of the rate data for nine gasification tests using Equation (4). The results of this analysis are shown in Table 4. This table presents average results for individual species for an initial rate period for each type coal gasified. The ultimate yield values shown have been normalized to a unit coal basis.

The following observations can be drawn from Table 4.

1. The average ultimate yield of CH_4 for Illinois No.6 coal is approximately 2.7 scf CH_4/lb coal maf which is in good agreement with a value of 2.4 scf CH_4/lb coal maf which would be obtained by extrapolating the data for the SYNTHANE gasifier to 200 psig.
2. The kinetic parameters for the initial rate period are for the most part fairly consistent within a given coal type. For example, for Wyoming coal the rate constants range from 0.149 to 0.173 min^{-1}. In the worst case (Illinois No.6 coal), the rate constants vary by a factor of four which is still in fair agreement considering the assumptions made in the analysis and errors involved in computing production rates. Wyoming subbituminous coal appeared on the average to have the highest specific rate of product formation (i.e., largest rate constants) of any of the coals tested.
3. The values of the rate constants for the different coals and each component are close to each other with a simple average constant being approximately 0.10 min^{-1}.
4. Examination of the average ultimate yields for the various coals in Table 4 shows that the bituminous coals have the greatest potential for the production of CH_4 and C_6H_6 as well as the sulfur-containing species. The potential for sulfur species production appears to roughly parallel the sulfur content of the coal except for COS in the case of Illinois No.6. However, only one value of the ultimate COS yield could be computed out of the three Illinois runs, and this may not be representative. Of the lower ranked coals, the Wyoming subbituminous coal had the highest potential for CH_4 and C_6H_6 product with ultimate yields of these components approximately on the same order as the Illinois No.6 bituminous coal.

CONCLUSIONS

Screening tests in which several types of coal were gasified have been considered in this paper. Major emphasis has been placed on the analysis of temperature histories in the gasifier bed and transient production rates of the major gas products, minor hydrocarbons, and selected sulfur-containing species.

The temperature in the bed was found to be dominated by the gasifier furnace when the furnace was in operation. The rate of increase in the average bed temperature in the gasifier after the coal drop appeared to be

TABLE 4. AVERAGE KINETIC PARAMETERS FOR THE INITIAL RATE PERIOD

Volatile Species	Kinetic Parameters									
	Illinois No.6 Coal		Western Kentucky*		Montana*		Wyoming		Zap North Dakota	
	k_1, min^{-1}	V_∞, sℓ/kg coal	k_1, min^{-1}	V_∞, sℓ/kg coal	k_1, min^{-1}	V_∞, sℓ/kg coal	k_1, min^{-1}	V_∞, sℓ/kg coal	k_1, min^{-1}	V_∞, sℓ/kg coal
CH_4	0.080	141.0	0.155	243.0	0.103	63.3	0.149	121.0	0.064	67.8
C_6H_6	0.088	3.05	0.095	4.28	0.092	1.32	0.165	2.55	0.108*	0.70*
H_2S	0.047	11.5	0.101	10.2	0.104	0.93	0.164	1.80	0.087	1.16
COS	0.036*	0.027*	0.107	0.17	0.062	0.13	0.173	0.071	0.057	0.077
Thiophene	0.130	0.47	0.192	0.17	0.104	0.015	0.149	0.0093	0.046	0.0057

*Data available for only one gasification test.

k = rate constant for the initial kinetic period.

V_∞ = ultimate yield.

be proportional to the difference between the average final temperature and the instantaneous average bed temperature.

According to the Gregory-Littlejohn equation, the coal bed temperature should have a significant effect on evolution of total volatile material. At a constant heating rate the Gregory-Littlejohn equation predicts that a semilog graph of the devolatilization rate as a function of time should be linear during the initial stages of the gasification test. This behavior was observed for the evolution of individual components such as methane, benzene, minor hydrocarbons, and sulfur species indicating the possibility of developing a Gregory-Littlejohn type of equation for each volatile species.

A simple kinetic model, which has been widely used in the literature in one form or another, was applied to rate-time data for selected chemical components. This model assumes that the rate of formation of a species is proportional to the potential amount of that species remaining in the coal. The model involves two parameters: (1) the ultimate yield of the species, and (2) a proportionality (kinetic rate) constant. It was found that the kinetic rate constant was roughly the same for all species and all coals with a simple average of the constants being 0.10 min^{-1}.

The average ultimate yield for each coal for a given species was dependent on the chemical species and coal type. The ultimate yield of methane and benzene approximately paralleled the volatile content of the coal and yield of sulfur-containing components paralleled the sulfur content of the coal. The potential for the evolution of sulfur-containing compounds into the gas was found to be an order of magnitude less for the subbituminous and lignite coal than for the bituminous coals.

ACKNOWLEDGEMENT

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CARBON CONVERSION, MAKE GAS PRODUCTION, AND FORMATION OF SULFUR GAS SPECIES IN A PILOT-SCALE FLUIDIZED BED GASIFIER

by

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R. M. Felder, S. Ganesan, and R. M. Kelly

ABSTRACT

The steam-oxygen gasification of a pretreated Western Kentucky No. 11 bituminous coal was carried out in a pilot-scale fluidized bed gasifier. This paper describes the experiments and summarizes measured carbon conversions, sulfur conversions, make gas production rates, and the results of material balance calculations on total mass and major elements (C, H, O, N, and S). The development of a single stage kinetic model for the gasifier is outlined, and correlations of the experimental results using this model are presented. Quantities of sulfur gas compounds formed in the gasifier at different operating conditions are summarized and a first analysis of these results is presented.

INTRODUCTION

Since 1976, the Department of Chemical Engineering at North Carolina State University has been engaged in a research project on coal gasification sponsored by the U. S. Environmental Protection Agency. The facility used for this research is a small coal gasification-gas cleaning pilot plant. The overall objective of the project is to characterize the gaseous and condensed phase emissions from the gasification-gas cleaning process, and to determine how emission rates of various pollutants depend on adjustable process parameters. Specific tasks to be performed are:

1. Identify and measure the gross and trace species concentrations in the gasifier product streams.

2. Correlate measured emission levels with coal composition and gasifier operating variables.

3. Perform material balances around the gasifier, raw gas cleanup system, and acid gas removal system, and determine the extent to which selected species are removed from the synthesis gas in each subsystem.

4. Correlate measured extents of conversion and removal efficiencies for various species with system operating variables.

5. Evaluate and compare the performance characteristics of alternative acid gas removal processes.

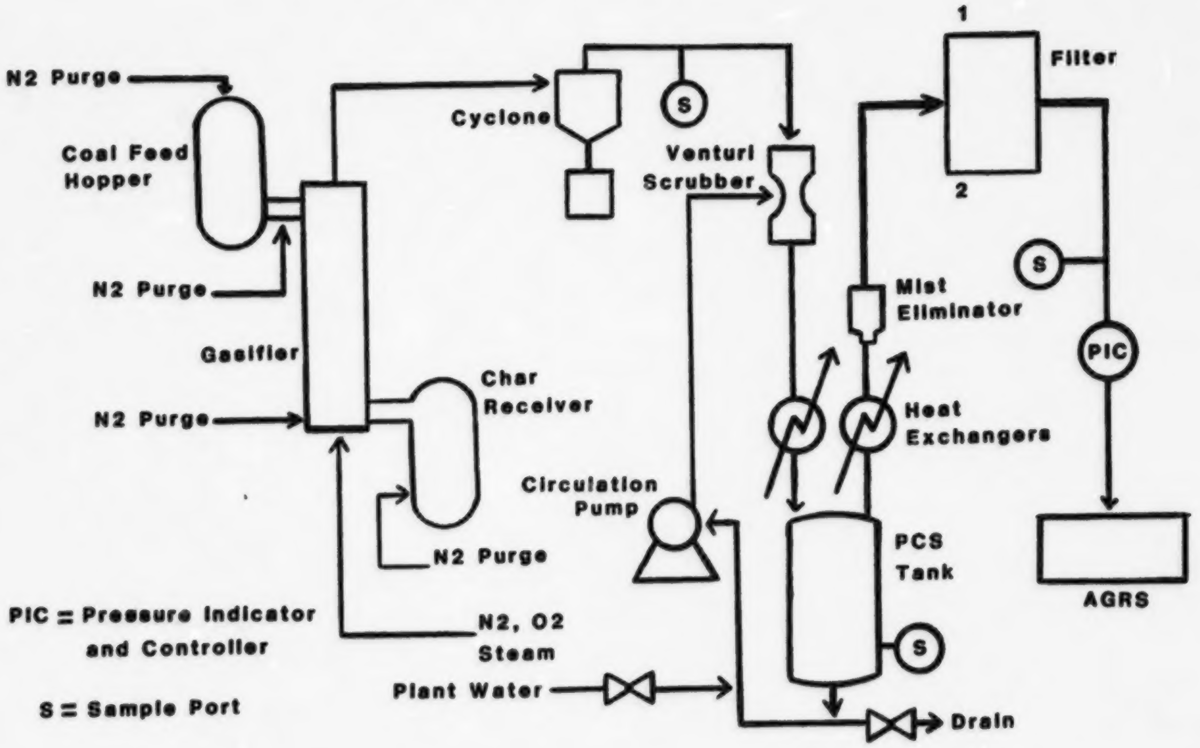
6. Use results to develop models for the gasification and gas cleanup processes.

A complete description of the facility and operating procedures is given by Ferrell et al., Vol I, (1980), and in abbreviated form by Felder et al. (1980). A schematic diagram of the Gasifier and Particulates, Condensables, and Solubles (PCS) removal system is shown in Figure 1. The Acid Gas Removal System (AGRS) is an integtral part of the facility, but will not be discussed here.

In the initial series of runs on the gasifier, a pretreated Western Kentucky No. 11 coal was gasified with steam and oxygen. A computer program was written to reduce the operating and analytical data for a run to manageable proportions and to perform material balance calculations. In addition, a single-stage model for the gasifier was formulated and used to correlate the results of the char gasification runs. This paper outlines the data processing program, describes the modeling and model parameter estimation procedures, presents the char gasification results and comparisions with model predictions, and presents a preliminary analysis of the formation of sulfur gases in the gasifier.

FIGURE 1

GASIFIER - PCS SYSTEM


N2 Purge
Coal Feed Hopper
N2 Purge
Gasifier
N2 Purge
Char Receiver
N2 Purge
N2, O2 Steam
Cyclone
S
Venturi Scrubber
Circulation Pump
Plant Water
1
Filter
2
S
Mist Eliminator
PIC
Heat Exchangers
PCS Tank
S
Drain
AGRS
PIC = Pressure Indicator and Controller
S = Sample Port

DATA REDUCTION COMPUTER PROGRAM

A complete description of the data reduction program is given by Ferrell et al., Vol II, (1980). The program takes as input the reactor temperature profile and pressure, bed dimensions, solid feed properties (sieve analysis, density, settled bed density, proximate and ultimate analyses), feed rates of coal, steam, oxygen and nitrogen, removal rate of char, reactor leak rate, gas flow rate at the PCS system outlet, masses of coal fed, spent char collected, cyclone dust collected, ultimate analyses of the spent char and cyclone dust, chromatographic analyses of the gases exiting the cyclone and the PCS system, pressure drop across a 20-inch segment of the bed, various feed and effluent flow meter calibration temperatures and pressures, and results of trace element and wastewater constituent analyses.

The output of the program contains the following components:

1. Reactor specifications, including the average bed temperature and pressure, the apparent bed density and void fraction, and the bed expansion factor.

2. Solid feed properties, including coal type, solid particle and settled bed densities, as-received moisture content, average feed particle diameter, and proximate and untimate analyses.

3. Feed rates of coal, steam, oxygen, and nitrogen, selected feed ratios and inlet conditions, superficial gas velocity, solids holdup, and space times for both gases and solids.

4. The make gas flow rate and chemical composition.

5. Production rates of fuel components and the heating value of the make gas.

6. Carbon, steam, and sulfur conversions.

7. Material balances on total mass, and on carbon, hydrogen, oxygen, nitrogen, and sulfur.

8. An energy balance.

9. Results of water analyses.

10. Results of trace element analyses and trace element material balances.

An example of the partial output for a run made on January 22, 1980, is shown in Table 1.

Table 1

```
****************************************
*                                      *
* NCSU DEPARTMENT OF CHEMICAL ENGINEERING *
*                                      *
* FLUIDIZED BED COAL GASIFICATION REACTOR *
*                                      *
****************************************

                    RUN GO-44B  1/22/80  11:15-14:30


       REACTOR SPECIFICATIONS                          FEED RATES AND RATIOS

PRESSURE     = 101.6 PSIG ( 801.7 KPA)           COAL      = 34.69 LB/HR (15.74 KG/HR)
TEMPERATURE  = 1699.8 DEG.F ( 926.5 DEG.C)       STEAM     = 55.85 LB/HR (25.33 KG/HR)
BED HEIGHT   = 38.0 IN. (0.97 METERS)            OXYGEN    = 10.10 LB/HR ( 4.58 KG/HR)
BED DIAMETER =  6.0 IN. (0.152 METERS)           NITROGEN  =  6.32 LB/HR ( 2.87 KG/HR)
ESTIMATED BED VOIDAGE = 0.74                     PURGE N2  = 14.16 LB/HR ( 6.42 KG/HR)
SOLIDS HOLDUP = 18.4 LB ( 8.3 KG)                STEAM/CARBON = 1.31 MOLES STEAM/MOLE C
                                                 O2/CARBON    = 0.13 MOLES O2/MOLE C
                                                 N2/O2        = 0.71 MOLES N2/MOLE O2


                 ELEMENTAL MATERIAL BALANCES : FLOWS IN LB/HR

                  MASS      C       H       O       N       S

          COAL    34.7    28.44    0.16    1.37    0.05   0.918
         GASES    86.4     0.00    6.25   59.70   20.47   0.000
   TOTAL INPUT   121.1    28.44    6.41   61.06   20.52   0.918

          CHAR    21.8    18.10    0.08    0.53    0.08   0.412
          DUST     1.8     1.20    0.01    0.23    0.01   0.029
         GASES    96.2     8.99    6.43   59.88   20.43   0.426
    WASTEWATER     0.0     0.00    0.00    0.00    0.00   0.000
  TOTAL OUTPUT   119.8    28.29    6.52   60.64   20.52   0.866

  % RECOVERY     98.9%    99.5%  101.8%   99.3%  100.0%   94.3%



                                         EXPERIMENTAL    MODEL

  CARBON CONVERSION (PERCENT)
     COMBUSTION                                           14.0
     GASIFICATION                                         18.7
     TOTAL                                   31.6         32.7

   DRY MAKE GAS FLOW RATE (SCFM)             11.7         12.0

   HEATING VALUE OF SWEET GAS (BTU/SCF)     296.0        286.1

   EFFLUENT FLOW RATES (LB/HR)
             CO                              8.48         8.67
             H2                              0.94         1.00
             CH4                             0.66         0.41
             CO2                            17.79        19.33
             N2                             20.43        20.48
             H2S                             0.434        0.297
```

GASIFIER MODEL

To aid in the analysis of the char gasification runs, a mathematical model of the fluidized bed gasifier was developed. The model takes as input the average reactor bed temperature and pressure, bed dimensions, feed rates of coal, steam, oxygen, nitrogen, and purge nitrogen, solids holdup, ultimate analysis of the feed coke and spent char, and values of three adjustable model parameters, the relative reactivity of the coke, the CO/CO2 distribution coefficient, and the water gas shift reactivity parameter.

MODEL DEVELOPMENT AND ASSUMPTIONS

The model treats the gasifier as a single perfect mixer, with the following six reactions taking place:

$$C + H_2O = CO + H_2 \qquad (1)$$

$$C + 2H_2 = CH_4 \qquad (2)$$

$$2C + H_2 + H_2O = CO + CH_4 \qquad (3)$$

$$CO + H_2O = CO_2 + H_2 \qquad (4)$$

$$C + 1/2O_2 = CO \qquad (5)$$

$$C + O_2 = CO_2 \qquad (6)$$

Reactions 5 and 6 are the oxidation steps required to supply heat for the remaining reactions. These two reactions are assumed to occur instantaneously in a zone of negligible volume separate from the gasification zone. All oxygen in the feed gas is assumed to be consumed to form CO and CO2 according to the relation

$$C + aO_2 = (2-2a)CO + (2a-1)CO_2 \qquad (7)$$

where "a", the combustion product distribution parameter, is an adjustable parameter. A value of a = 0.5 indicates that all CO is formed, while a value of a = 1.0 indicates that only CO2 is formed.

Reactions 1, 2, and 3 are the reactions by which Johnson (1974) at the Institute of Gas Technology correlated gasification kinetics. Reaction 1 is the conventional steam-carbon reaction. Reaction 3 is assumed to be an independent reaction, although it is attainable as a linear combination of 1 and 2.

The correlation used by Johnson to describe the carbon conversion is given by

$$r = f_L k_T (1-f_c)^{2/3} \exp(-bf_c) \qquad (8)$$

where r is the rate at which the carbon is gasified, k_T is the sum of the rate constants for Reactions 1, 2, and 3, f_c is the fractional carbon conversion and b is a kinetic parameter which depends on gas composition and pressure. Expressions for k_1, k_2, and k_3 are presented by Ferrell et al., Vol II. (1980).

The relative reactivity factor f_L is determined from

$$f_L = f_0 \exp(8467/T_0) \qquad (9)$$

where T is the maximum temperature to which the char has been exposed prior to gasification. The relative reactivity factor, f_0, which is an adjustable parameter whose values depend on the particular char used, has values ranging from 0.3 for low-volatile bituminous coal chars to about 10 for North Dakota lignites (Johnson, 1974).

Reacton 4 is the water gas shift reaction, often assumed to be at equilibrium in gasification processes. Results to be described indicate this may be a bad assumption, leading to the necessity of incorporating shift kinetics into the model. The rate expression used is that given by Wen and Tseng (1979)

$$r_4 = 1.6652 \times 10^4 V(1-e) f_{wg} \exp(-25147/T)\ P\ G \qquad (10)$$

where

V = bed volume
$G = [CO] - [H_2][CO_2]/[H_2O][K_4]$
e = bed void fraction
f_{wg} = adjustable shift reactivity parameter (varies from char to char)
K_4 = equilibrium constant

The equilibrium constants for the water gas shift reaction and for reactions 1, 2, and 3 were taken from Lowry (1963), and were fit to the equation

$$\mathrm{Ln}\ (K_E) = (a_0/T) + a_1 \qquad (11)$$

by least-squares analysis (Alexander, 1978).

A complete description of the model development and the reactor simulation computer program is given by Ferrell et al., Vol II, (1980).

CHAR GASIFICATION RESULTS

A total of 56 runs have been completed using a Western Kentucky No. 11 coal char as feed stock. The first 13 of these runs were used primarily for the development of operating and sampling procedures, and refinement of analytical methods. The data from gasifier runs GO-14 through GO-56 have been collected and reviewed, and a complete analysis of these runs is presented by Ferrell et al., Vol II, (1980).

MASS BALANCES

An example of a single page output from the previously described data processing program is shown as Table 1. Criteria for acceptance of a run were arbitrarily chosen following inspection of the mass balance results. A run is judged acceptable if the total mass recovery is within 5% of 100%, and if the worst of the recoveries of elements C, H, and O are within 8%. Based on these criteria, 22 of the 34 runs reviewed are acceptable, and are designated by crossed circles in the figures. Points with filled circles are for runs with total mass recoveries within 5% and worst element recoveries within 6%. Open circles are used for all other runs.

TEMPERATURE EFFECTS

The effect of the average bed temperature on the dry, nitrogen-free make gas flow rate is shown in Figure 2. For the points shown, the molar steam to carbon ratio varied from 0.92 to 1.15. The plot indicates that the make gas flow rate is highly sensitive to the average bed temperature, with scatter due mainly to the small steam to carbon ratio differences and differing feed rates. The high sensitivity makes determination of the average bed temperature crucial for good model predictions.

STEAM TO CARBON EFFECTS

The effect of the steam to carbon ratio on the make gas flow rate is shown in Figure 3. At any given temperature the effect of increasing the steam rate at a given carbon input is to increase the make gas flow rate. A side benefit to operating with relatively high steam to carbon ratios in the fluidized bed gasifier is a reduced tendency for the char to clinker.

SULFUR CONVERSION

Measured sulfur conversion, assumed to equal the carbon conversion by the model, is plotted vs carbon conversion in Figure 4. In most cases the sulfur conversion is greater than the carbon conversion. Studies are currently under way to put the sulfur gas evolution

FIGURE 2

THE EFFECT OF THE AVERAGE BED TEMPERATURE ON THE MAKE GAS FLOW RATE (DRY, N_2 FREE)

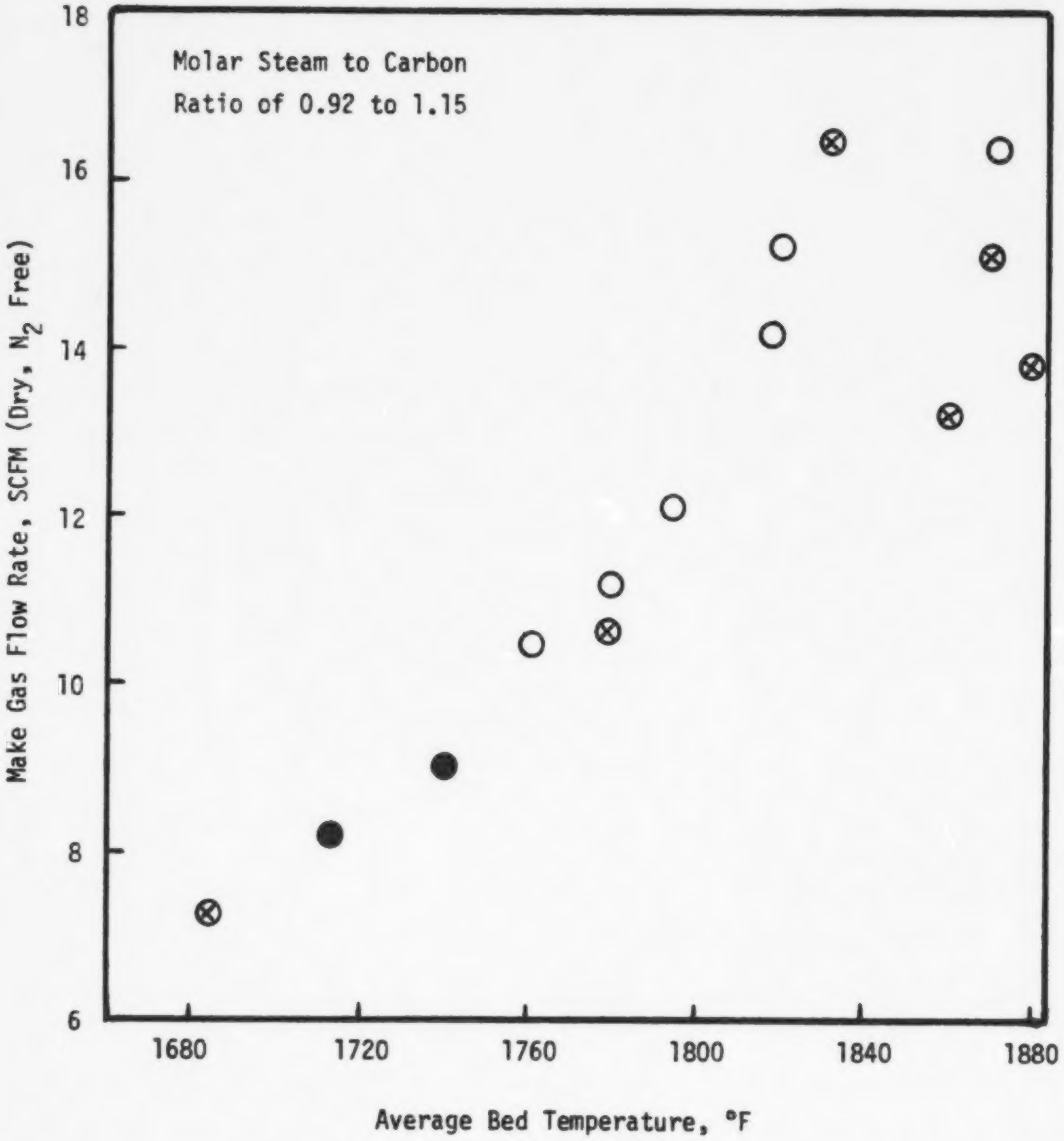


FIGURE 3

THE EFFECT OF THE STEAM TO CARBON RATIO ON THE MAKE GAS FLOW RATE (DRY, N_2 FREE)

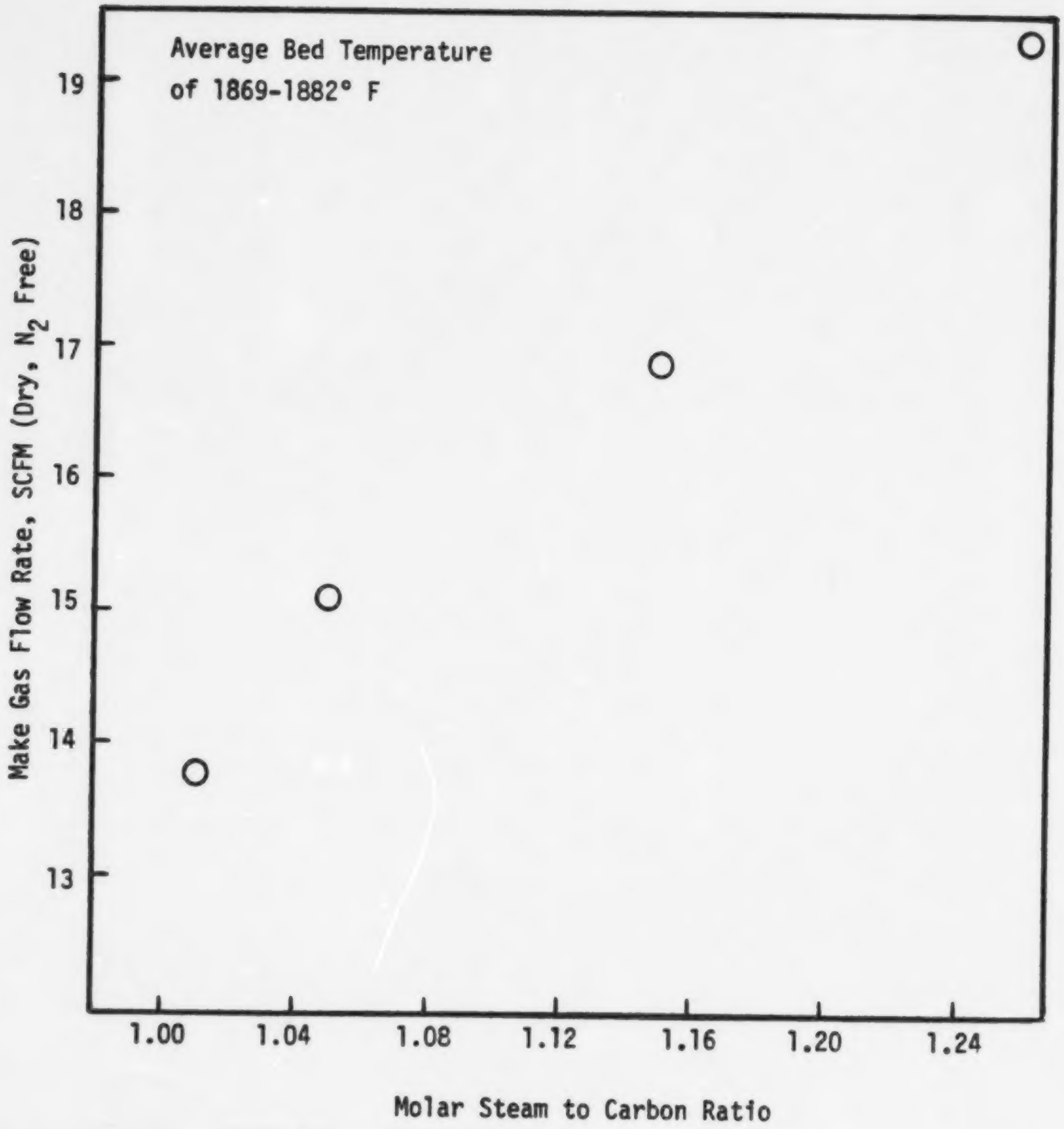
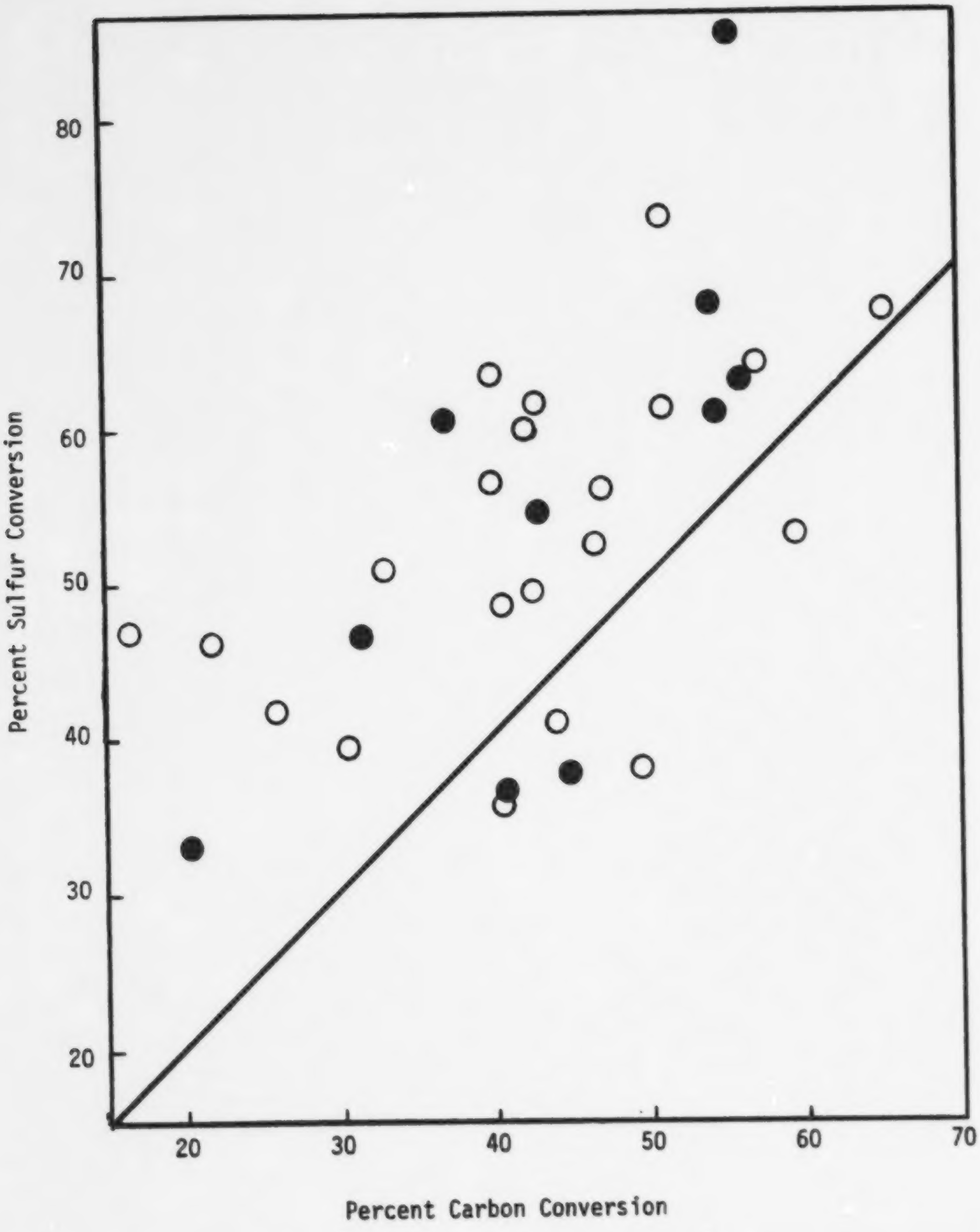


FIGURE 4

COMPARISON OF PERCENT SULFUR CONVERSION TO PERCENT CARBON CONVERSION



on a firmer theoretical foundation.

EVALUATION OF MODEL PARAMETERS

In its present form, the model has three adjustable parameters:

1. the char reactivity, f_0
2. the combustion product distribution parameter, a, which specifies the split between CO and CO2 in the products of the combustion stage of the gasification
3. the water gas shift reactivity parameter, f_{wg}.

These parameters were evaluated by using a Pattern Search algorithm to minimize a function of the sum of squared deviations between predicted and measured values of gasifier performance variables. This analysis gave the following values:

1. $f_0 = 0.50$
2. $a = 0.95$
3. $f_{wg} = 0.0000099$

The value of a, when substituted into Eg. 7, indicates that 90% of the carbon oxidized forms CO2 and 10% forms CO. An equation by Arthur (1951) predicts values of 0.57 at 1400 F to 0.52 at 2000 F, while several gasification studies have assumed a = 1.0.

Johnson (1975) developed a correlation for char reactivity

$$f_0 = 6.2\, y\, (1-y) \qquad (12)$$

where y is the dry, ash free carbon fraction in the original raw coal. Eq. 12 predicts a value of f = 1.1, which is larger than that determined in this study. The difference may be due to the differences in the microbalance used by Johnson and the fluidized bed of this study.

The value of $f_{wg} = 0.0000099$ indicates that the shift reaction rate is approximately five orders of magnitude less than the rate obtained in catalytic shift reactors. Wen and Tseng (1979) used a shift reactivity value of 0.00017 in modeling the gasification of a bituminous coal by the SYNTHANE process. The larger value used by Wen and Tseng may be attributed to the differences between the coal of their study and the char used in this study.

Due to the simplicity of the model, it is also likely that the effects of factors not specifically accounted for in the model have influenced the optimal values of the three model parameters. The values of the parameters found as described above appear to be reasonable, and are probably a fair representation of what actually happens in the fluidized bed gasifier.

MODEL RESULTS

Using the optimal parameter values, the model was run for gasifier runs GO-14 through GO-56. A representative model output is shown for run GO-44B in Table 2. Plots of predicted vs measured values of carbon conversion, dry make gas flow rate, and sweet gas heating value are shown in Figures 5 - 7. The reasonably close proximity of most points to the 45 degree line is gratifying in view of the crudeness of the model. The proximity of the points corresponding to the "best" runs (from the standpoint of satisfying mass balances) is even more satisfying.

For each run, the ratio

$$K = [CO_2][H_2]/[CO][H_2O] \tag{13}$$

was calculated, where [ ] is the mole fraction of the evaluated species in the product gas. This quantity would equal the water-gas shift equilibrium constant at the reactor temperature if this reaction proceeded to equilibrium. A plot of the predicted vs experimental values of this ratio, K, is given in Figure 8. The substantial degree of scatter may be attributed to the simplicity of the model, and equally to the fact that the mole fractions which are the constituents of K are interdependent, so that an experimental error in one of them affects the values of the others.

The significance of this plot emerges when it is compared with Figure 9, which shows the values of K predicted assuming shift equilibrium. This assumption leads to the overprediction of K by as much as a factor of two, and lends support to the conclusion that the shift reaction should not be assumed to proceed to equilibrium.

FORMATION OF SULFUR GASES

One of the objectives of gasifier runs GO-43 through GO-59 was to investigate the production of sulfur gas species in the fluidized bed reactor. A summary of results is given in Table 3.

The coal char used in this study has a very low volatile matter, less than 2%, and it is very likely that most of the sulfur is present as pyritic sulfur. For this case, it has been postulated that during

Table 2

```
                    ********************************
                    *                              *
                    * WELL-MIXED CHAR GASIFICATION *
                    *                              *
                    *        MODEL RESULTS         *
                    *                              *
                    ********************************

                      GO-44B  1-22-80  11:15-14:30


 REACTOR SPECIFICATIONS                      FEEDRATES(LB/HR)

 BED PRESSURE(PSIG)      101.60              INLET CHAR              34.69
 BED TEMPERATURE(F)     1699.80              STEAM                   55.85
 SOLIDS HOLDUP(LB)        18.40              OXYGEN                  10.10
 BED HEIGHT(IN)           38.00              NITROGEN                 6.32
 BED DIAMETER(IN)          6.00              HYDROGEN                 0.00
 BED VOIDAGE               0.74              PURGE H2                14.16


 MODEL PARAMETERS                            FEED CHAR ANALYSIS(WT PERCENT)

 PRETREAT TEMP(F)       2000.00              CARBON                  82.00
 CHAR REACTIVITY         0.5000              HYDROGEN                 0.50
 COMBUSTION EXTENT       0.9500              OXYGEN                   3.90
 SHIFT REACTIVITY     9.900E-06              NITROGEN                 0.10
                                             SULFUR                   2.60
                                             ASH                     10.80



                                          MODEL    EXPERIMENTAL

          DRY GAS FLOW RATE (SCFM)        12.04       11.73

          STEAM CONVERSION                0.171       0.153

          CARBON CONVERSION
            COMBUSTION                    0.140
            GASIFICATION                  0.187
            TOTAL                         0.327       0.316

          ASH CONTENT OF CHAR             15.24       12.00

          CHAR REMOVAL RATE (LB/HR)       23.07       21.80


                        GAS COMPOSITION (MOLE PERCENT)

                                   MODEL   EXPERIMENTAL

                        CO          6.76        6.60

                        H2         10.85       10.11

                        CH4         0.56        0.89

                        CO2         9.59        8.82

                        N2         15.96       15.91

                        H2S         0.19 *      0.28

                        COS         0.00        0.01

                        H2O        56.08       57.38

                              (* ESTIMATED)
```

FIGURE 5

PREDICTED VS. EXPERIMENTAL CARBON CONVERSION

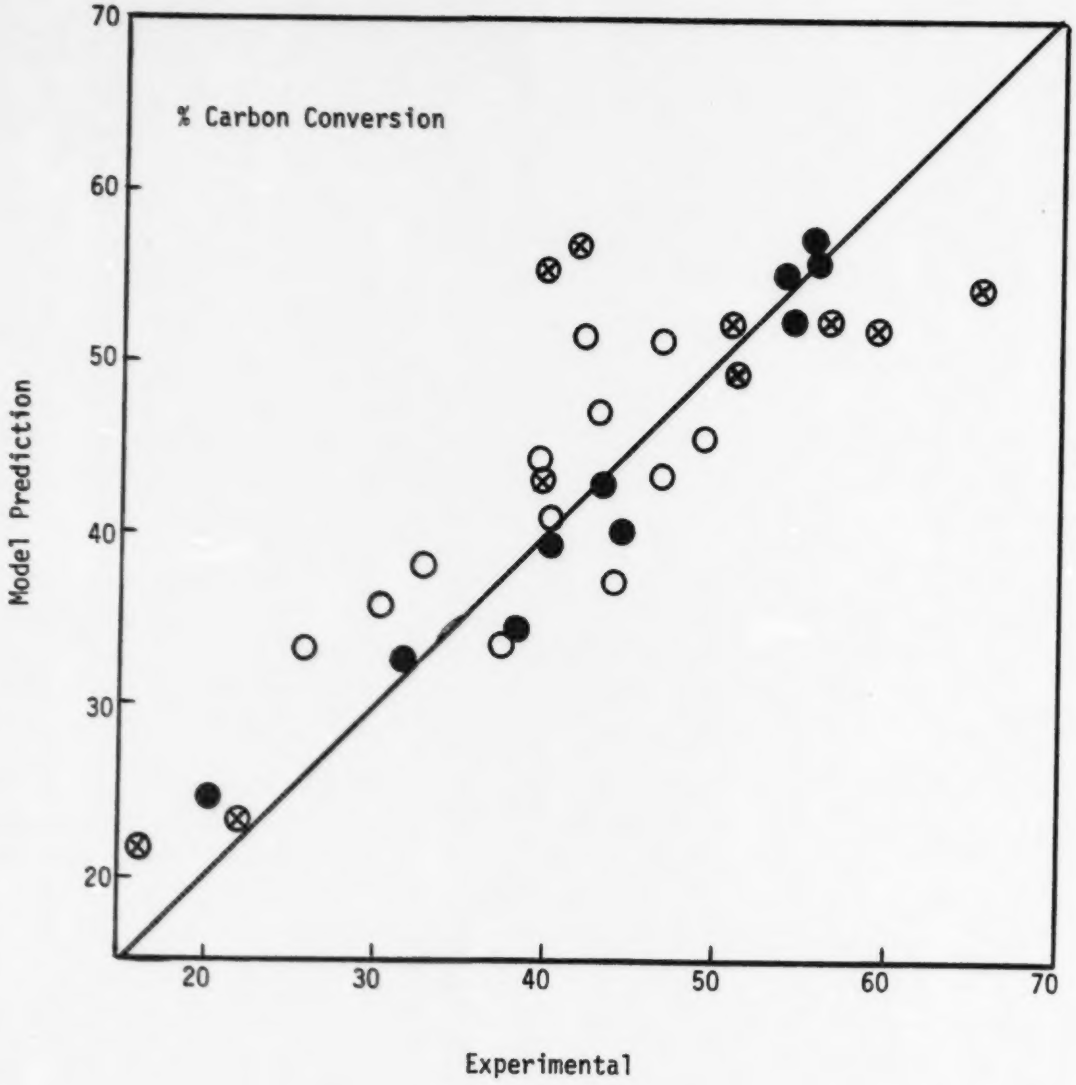


FIGURE 6

PREDICTED VS. EXPERIMENTAL DRY MAKE GAS FLOW RATE

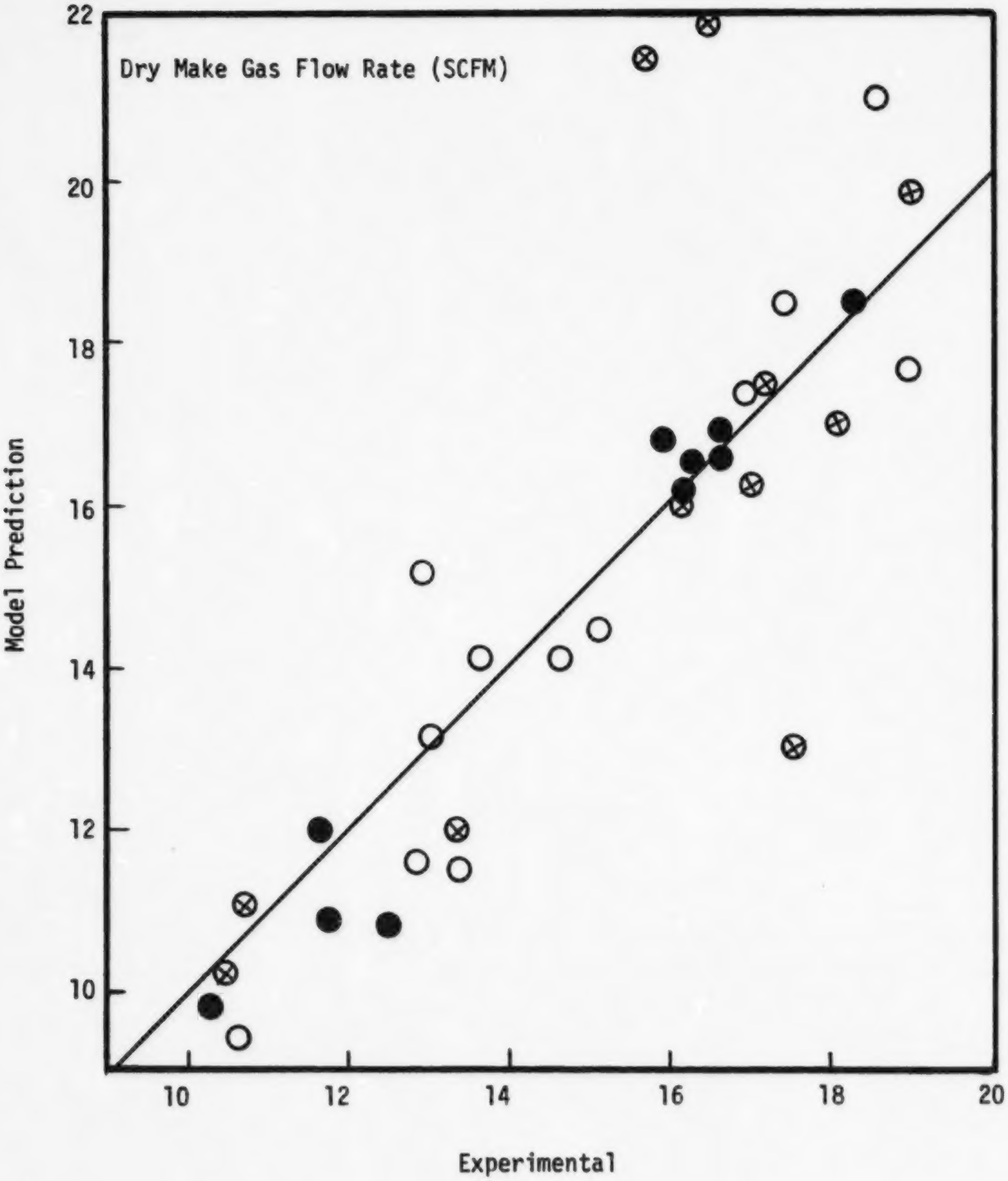


FIGURE 7

PREDICTED VS. EXPERIMENTAL HEATING VALUE OF SWEET GAS

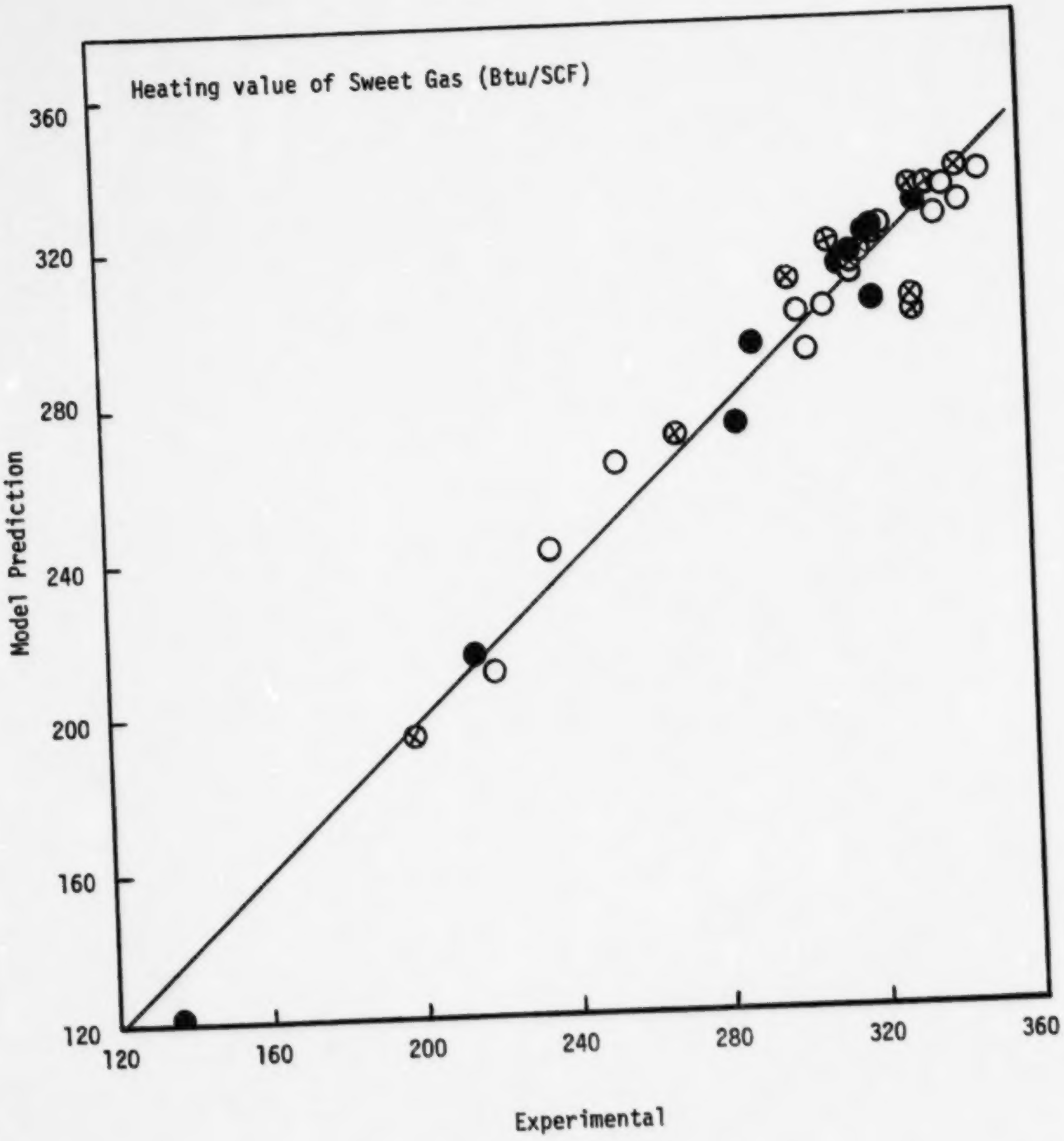


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FIGURE 8

PREDICTED VS. EXPERIMENTAL K VALUE

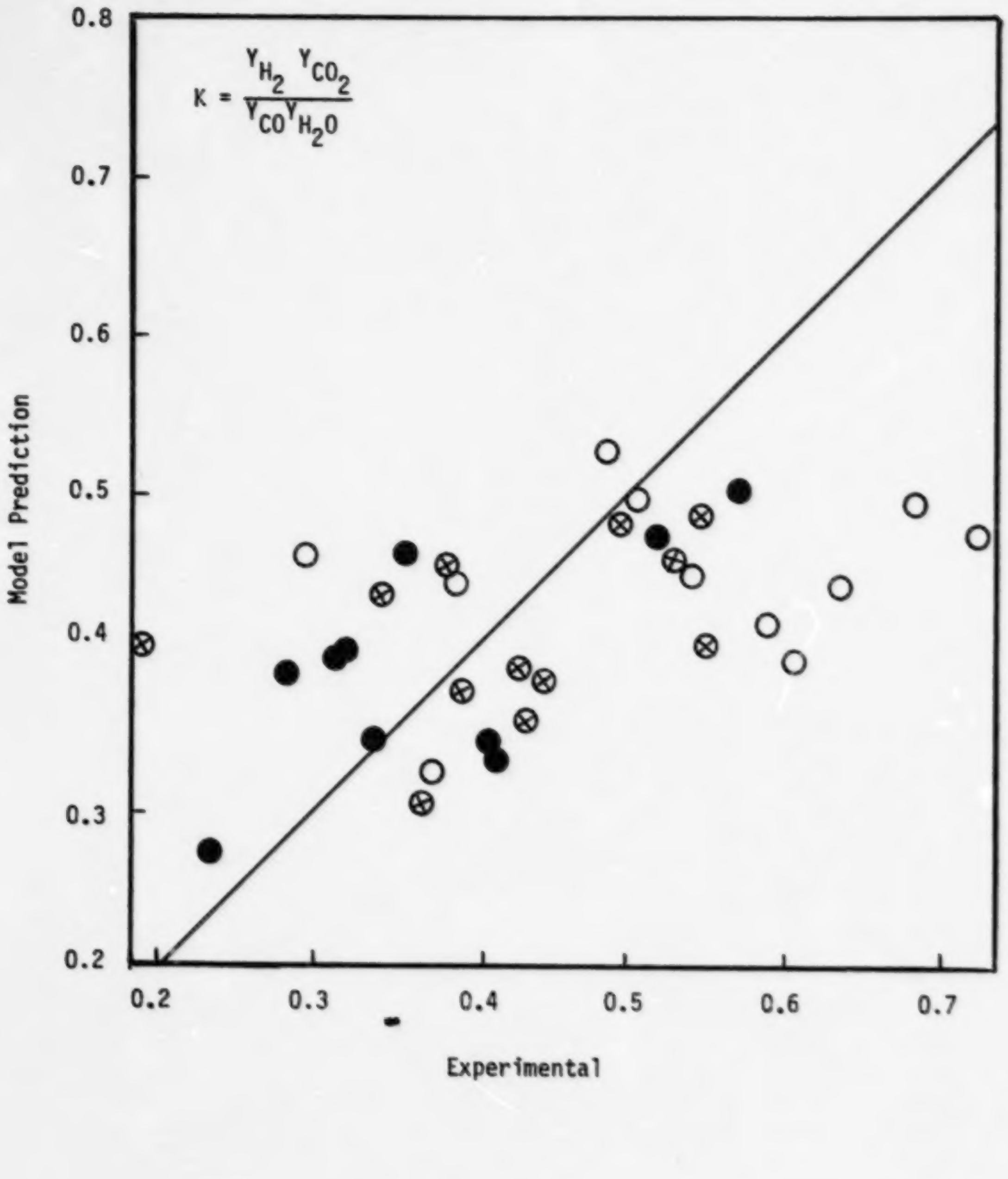


FIGURE 9

PREDICTED VS. EXPERIMENTAL K VALUE

ASSUMING SHIFT EQUILIBRIUM

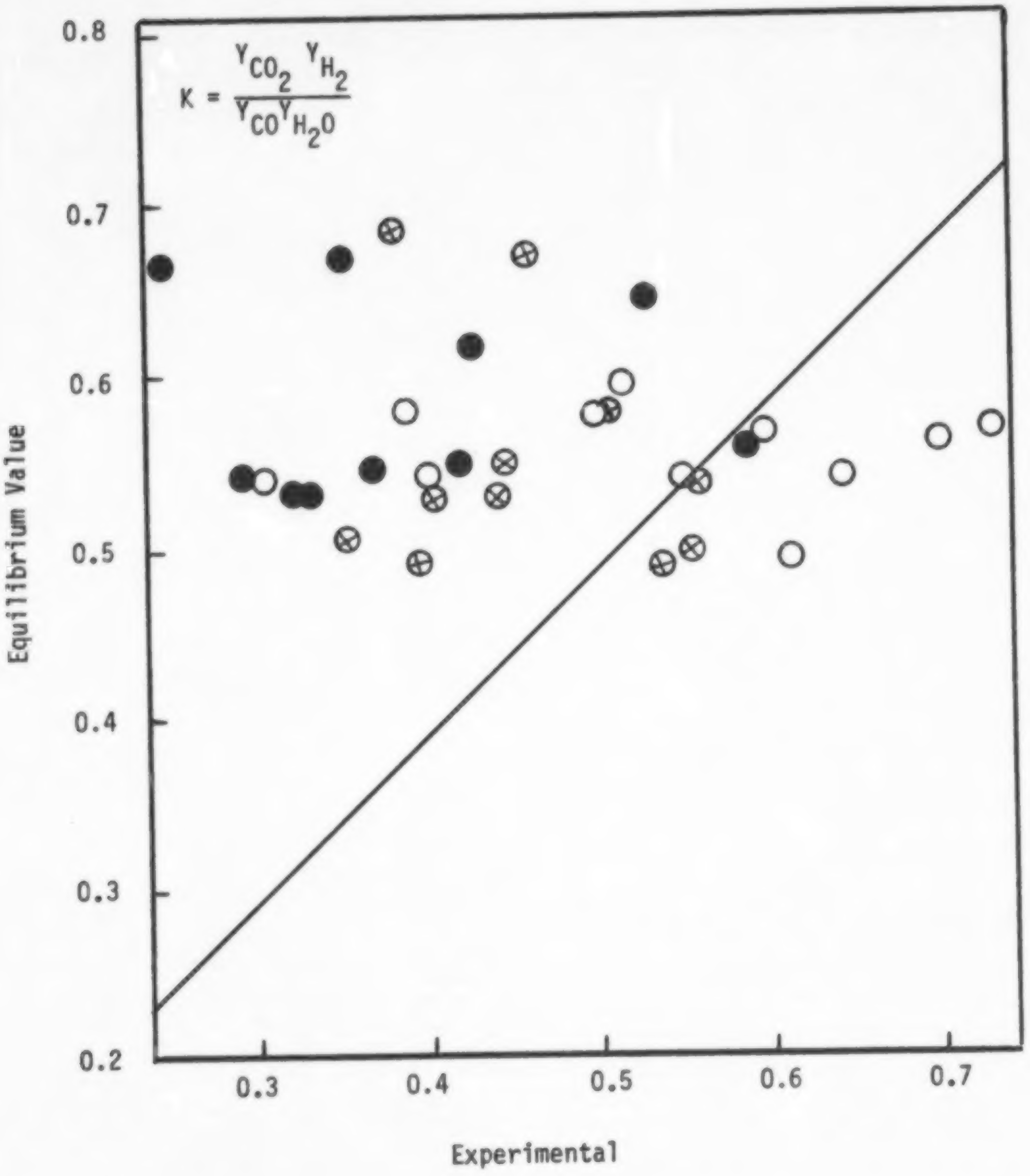


TABLE 3
CONCENTRATIONS OF SULFUR GASES IN REACTOR EFFLUENT

Run	Bed	Reactor Effluent Concentrations ppm				
No.	Temp. F	H_2S	COS	CS_2	Methyl Mercaptan	Thiophene
43	1794	6229	277	2.27	x	x
44	1678	6510	283	2.44	x	N.D.
45	1671	3433	266	7.92	x	x
46	1790	5478	222	1.56	x	x
47	1785	5071	272	1.97	x	x
48	1778	6912	312	3.30	x	x
49	1799	7052	403	3.80	x	x
51	1777	6711	299	1.56	x	x
55	1708	8931	465	2.95	x	x
56	1800	8924	410	1.58	x	N.D.
57	1778	8098	388	1.58	x	x
58	1771	5111	362	1.36	x	x
59	1803	8470	306	1.61	x	x

x - Less then 1 ppm
N.D. - Not detected

TABLE 3 CONTINUED
EQUILIBRIUM CONSTANTS FROM EXPERIMENTAL DATA

Run No.	Reactor Effluent Concentrations				Equilibrium Constants	
	CO	CO_2	H_2	H_2O	K_1	K_2
43	16.80	12.36	11.21	43.60	6.4	33.7
44	6.60	8.82	10.11	57.38	3.5	15.0
45	4.22	6.81	8.27	39.27	2.2	6.6
46	12.77	9.08	13.82	33.14	6.8	22.8
47	13.89	9.86	15.16	29.89	6.2	17.1
48	12.88	10.79	15.77	46.62	5.1	18.1
49	15.42	16.03	13.68	36.25	7.7	19.7
51	10.98	15.11	19.06	41.49	8.2	12.9
55	9.28	12.61	15.24	50.05	4.8	11.7
56	10.73	12.75	16.98	48.95	5.7	13.8
57	12.74	14.87	18.05	41.92	7.4	14.7
58	11.68	15.80	19.84	38.38	5.8	8.3
59	10.10	14.60	17.15	47.68	8.5	16.3

steam-oxygen gasification the gas-solid reactions form mainly hydrogen sulfide. The gas phase reactions then tend to bring the compounds CO2, H2O, H2, H2S, and COS to an equilibrium mixture.

The two gas phase reactions of most importance involving H2S and COS are:

$$COS + H_2O = H_2S + CO_2 \tag{14}$$

$$COS + H_2 = H_2S + CO \tag{15}$$

The equilibrium constants for these two reactions are defined as follows:

$$K_1 = [H_2S][CO_2]/[COS][H_2O] \tag{16}$$

$$K_2 = [H_2S][CO]/[COS][H_2] \tag{17}$$

where, due to the stoichiometry of the reactions, the brackets may indicate any convenient concentration. Ideal gas behavior is assumed.

A survey of the literature yielded several sets of equilibrium data for the above reactions, and several predictions based on thermodynamic data. Since there were substantial differences amoung the sources of data, predictions of the two equilibrium constants as funtions of temperature were derived from the data given in Reid et al. (1977). A least squares fit of the literature data, and the predicted curve from the data of Reid are shown in Figures 10 and 11.

Also shown on Figures 10 and 11 are calculated values of the equilibrium constants from the data in Table 3. Figures 12 and 13 show the experimental data on a expanded scale and a comparison of our data with the literature values given in Kohl and Riesenfeld (1979).

Although there is considerable uncertainty in determining the correct value of the equilibrium constants, and some inaccuracy in the experimental data, it appears that the sulfur compounds H2S and COS are in equilibrium with the major gases at the exit of the fluidized bed, and that the distribution of the sulfur gases between H2S and COS can be predicted if the sulfur conversion is known.

FIGURE 10

THE EQUILIBRIUM CONSTANT K_1

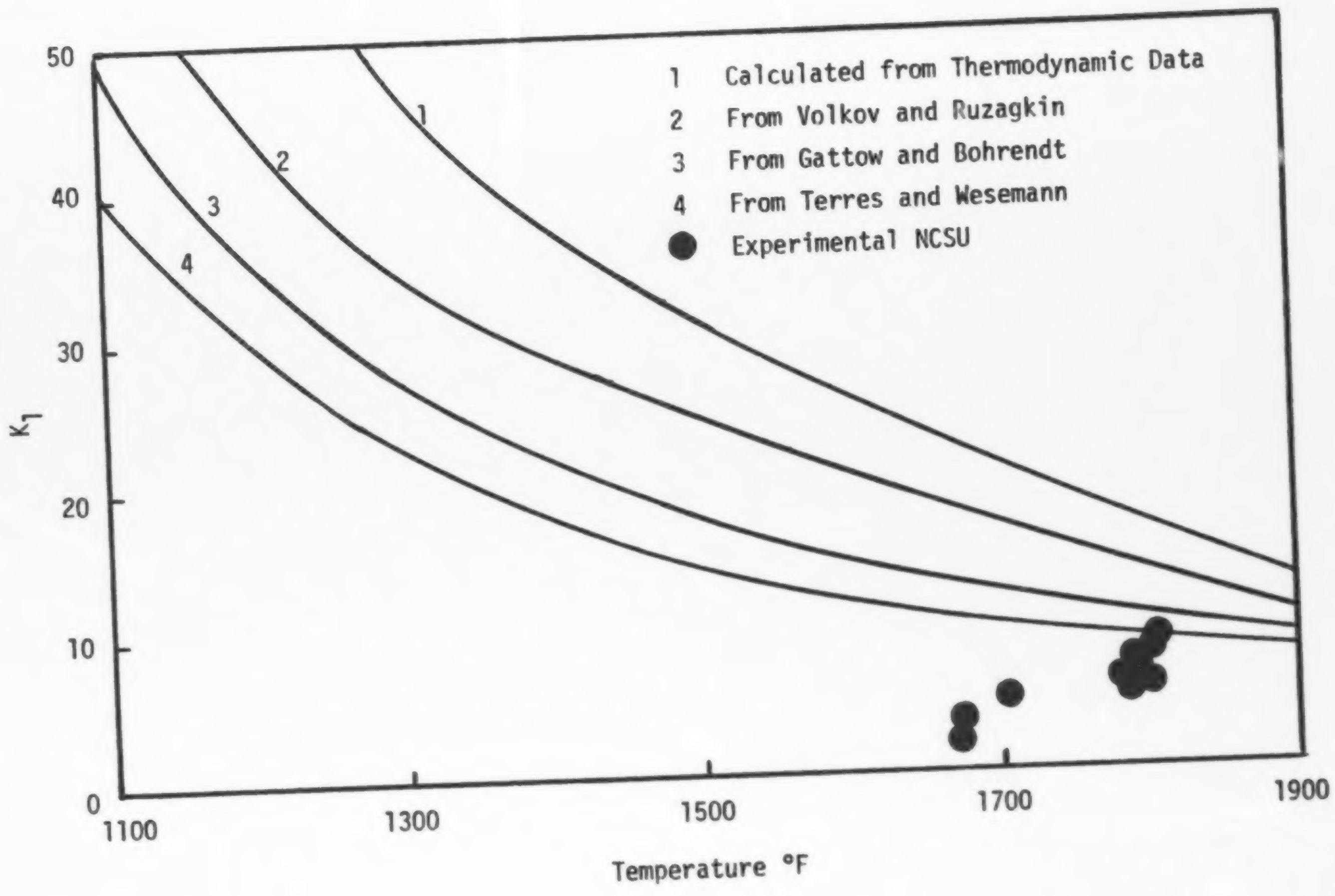


FIGURE 11

THE EQUILIBRIUM CONSTANT K_2

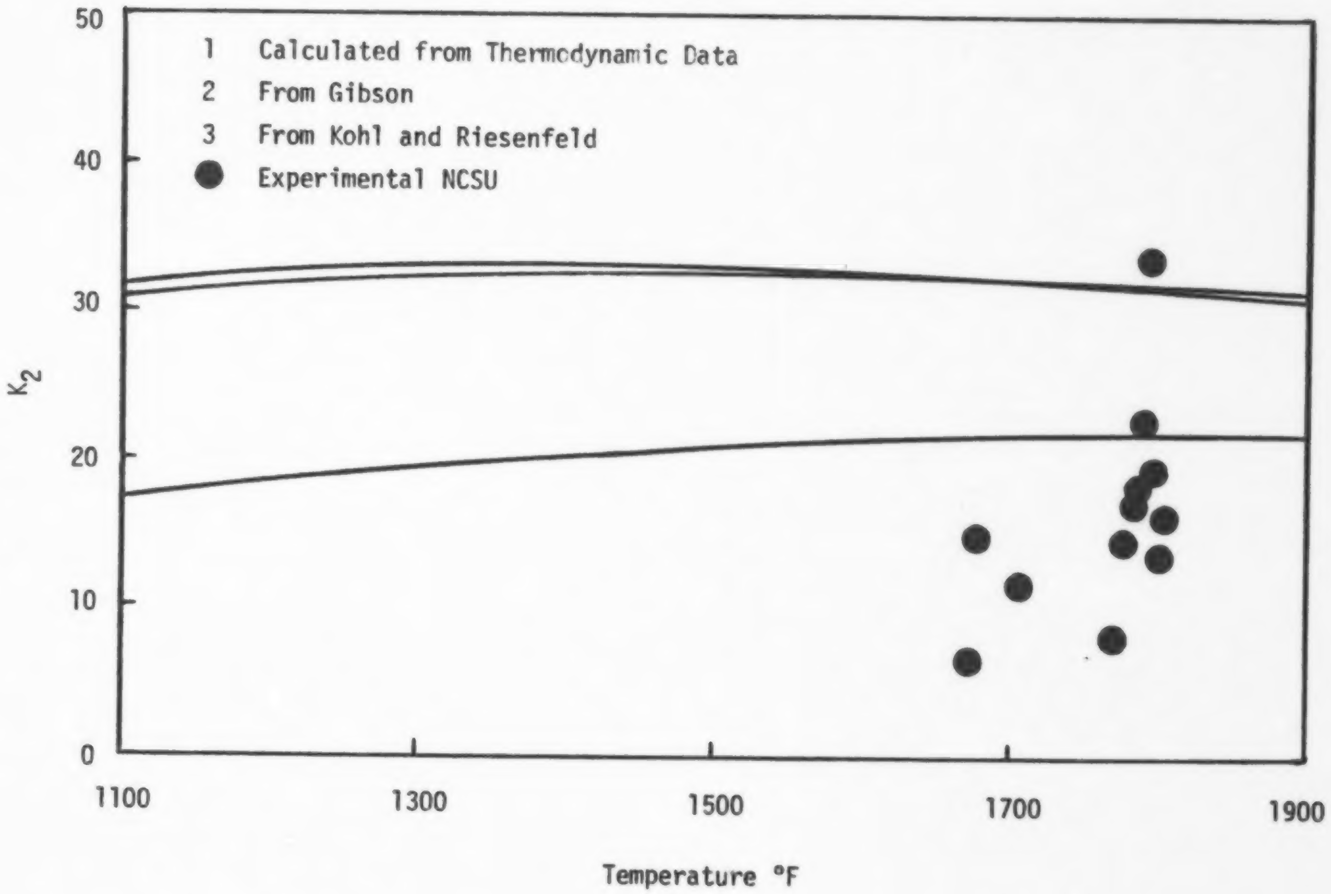


FIGURE 12

COMPARISON OF EXPERIMENTAL VALUES OF K_1 WITH DATA OF KOHL AND RIESENFELD

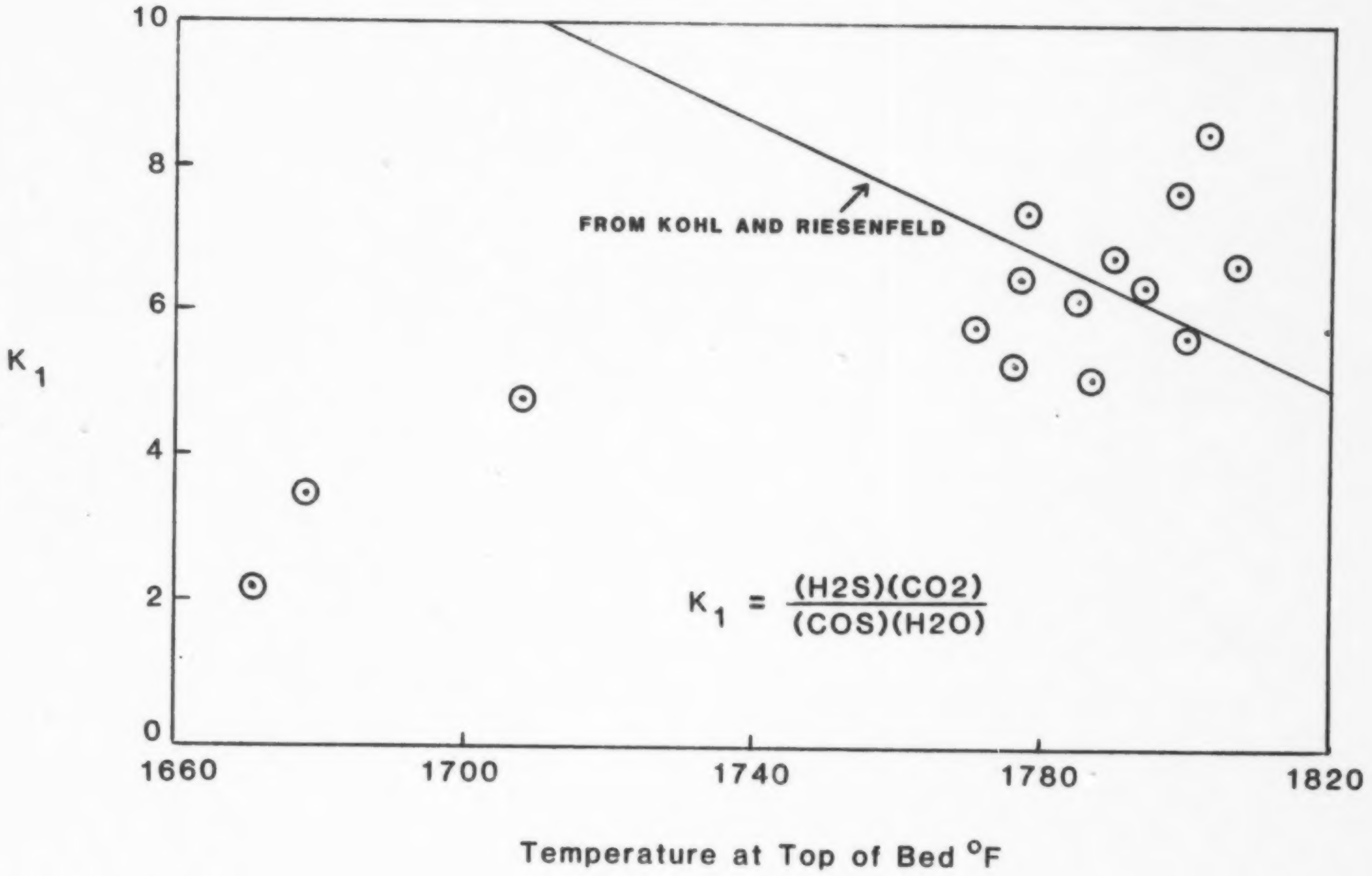
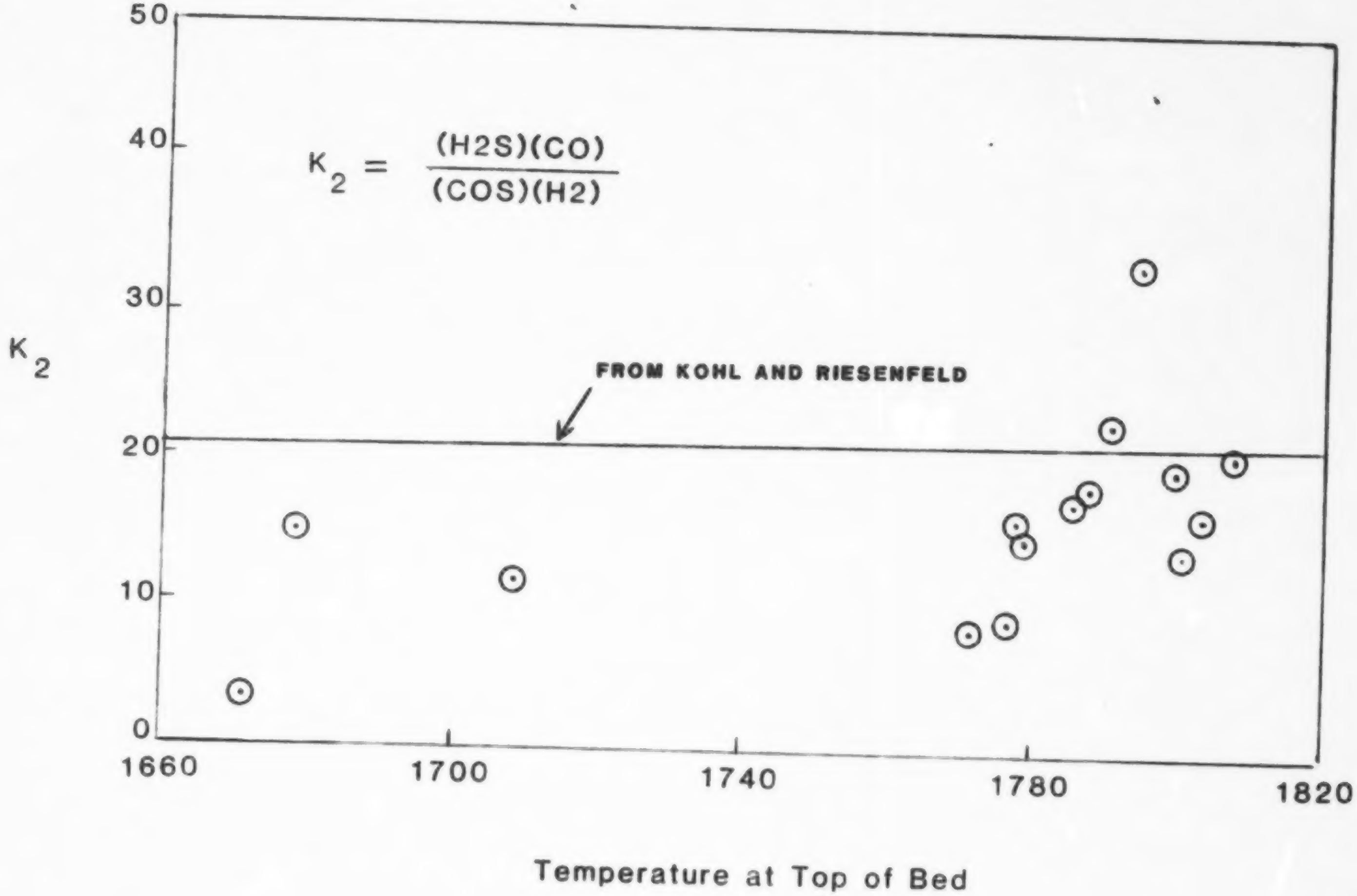


FIGURE 13

COMPARISON OF EXPERIMENTAL VALUES OF K_2 WITH DATA OF KOHL AND RIESENFELD



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MODDERFONTEIN
KOPPERS-TOTZEK
SOURCE TEST RESULTS

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ABSTRACT

A source test program was conducted at a Koppers-Totzek (K-T) coal gasification facility operated by AECI Limited at Modderfontein, Republic of South Africa. The EPA's interest in the K-T process stems from the fact that the process economics and demonstrated commercial reliability make it a very viable prospect for some U.S. applications. The responsibilities for sampling, analysis, and engineering descriptions of the Modderfontein plant were shared between TRW and GKT, Gessellschaft für Kohle-Technologie mbH of Essen, Federal Republic of Germany. GKT is the wholly owned subsidiary of the German-based parent company which is the developer and licensor of the K-T process. EPA's phased approach for environmental assessment was followed. Level 1 and Level 2 data were collected along with priority pollutant screening data. Much of the effort was focused on wastewater streams. The wastewater treatment, consisting of a clarifier and settling pond, was adequate to produce a final discharge that had lower pollutant levels than the fresh input waters supplied to the plant. The complete data are presented in this paper along with brief descriptions of the K-T process and the Modderfontein plant. The purpose of the Source Test and Evaluation was intended as an initial effort and was somewhat limited in scope.

MODDERFONTEIN KOPPERS-TOTZEK
SOURCE TEST RESULTS

INTRODUCTION AND SUMMARY

TRW, under contract 68-02-2635 to the Environmental Protection Agency, and at the direction of Project Officer William J. Rhodes, is performing the environmental assessment of high-BTU gasification and indirect liquefaction technologies. A major portion of this environmental assessment project is to obtain data on commercial operating facilities through Source Test and Evaluation (STE) programs. The ultimate objective of each STE program is to obtain the data necessary to: 1) evaluate environmental and health effects of waste streams or streams that may potentially be discharged in plants designed for U.S. sites, and 2) allow subsequent evaluation of the equipment available or required for controlling these streams. This paper describes an STE program that was conducted on a Koppers-Totzek (K-T) coal gasifier plant operated by AECI Limited in Modderfontein, Republic of South Africa. The EPA's interest in the K-T process stems from two principal factors: first, in the national drive to supplement liquid and gaseous fossil fuels through coal conversion, process economics dictate that the more viable conversion products will be those having the highest unit retail value. The K-T process represents one of the prime candidates for converting raw coal into the intermediate synthesis gas needed to produce these high-value products. Secondly, the K-T process has a lengthy history of successful application to a variety of foreign coals and promises to be equally adaptable over the range of American coals. This factor is particularly important in view of the contrasting lack of demonstrated commercial reliability on the part of the developmental U.S. gasifiers, and is viewed in a very positive light by both conversion project financiers and program managers.

The K-T process operates on an entrained bed principle. It utilizes a high temperature, atmospheric pressure reaction fueled by a continuous co-current input stream of coal, oxygen, and steam. The gasification reactor vessel is a horizontal, ellipsoidal, double-walled steel chamber with a refractory lining. Two gasifier designs are available. The two-burner gasifier design utilized at Modderfontein has a burner head located on each end of the ellipsoid as illustrated in Figure 1. The four-burner gasifier resembles two of the two-burner gasifiers which intersect one another at a 90^{0} angle. A burner head is located at each of the ends of the two intersecting ellipsoids. The gasifier operates with a flame temperature of 2000^{0}C (3650^{0}F) or more and a gas outlet temperature of about 1400^{0} to 1600^{0}C (2550^{0} to 2900^{0}F). The major constituents of the gasifier output stream are carbon monoxide and hydrogen.

All of the K-T gasification facilities in operation as of 1978 were used entirely to make synthesis gas as an input stream for the production of ammonia. The Modderfontein plant, illustrated in Figure 2, was commissioned in 1974 and has a design production rate of 1000 tonnes per day of ammonia. It utilizes a High Volatile B, Bituminous coal that is high in ash content (20%) and low in sulfur (1.0%).

The STE program was carried out as a joint effort between TRW and GKT. TRW's initial review of the Modderfontein plant resulted in the identification of 25 streams as necessary to the comprehensive STE goals. Of these 25 streams, nine were selected for testing as a result of discussions between GKT and TRW in which streams considered proprietary, not applicable, or otherwise restricted were eliminated from the list. The STE thus became limited in scope and focused on the nine available streams. Further STE programs are anticipated in the future which will serve to provide basic characterization data on K-T generated wastes so that control technology requirements for facilities built in the U.S. can be identified early in the planning stages. It is not intended that any data presented in this paper of future data resulting from tests at Modderfontein be used for the purpose of either promoting or criticizing specific process designs or operating practices of that facility. It should be stressed that each K-T plant is unique and that numerous design options exist for pollutant reduction within the process depending upon customer requirements.

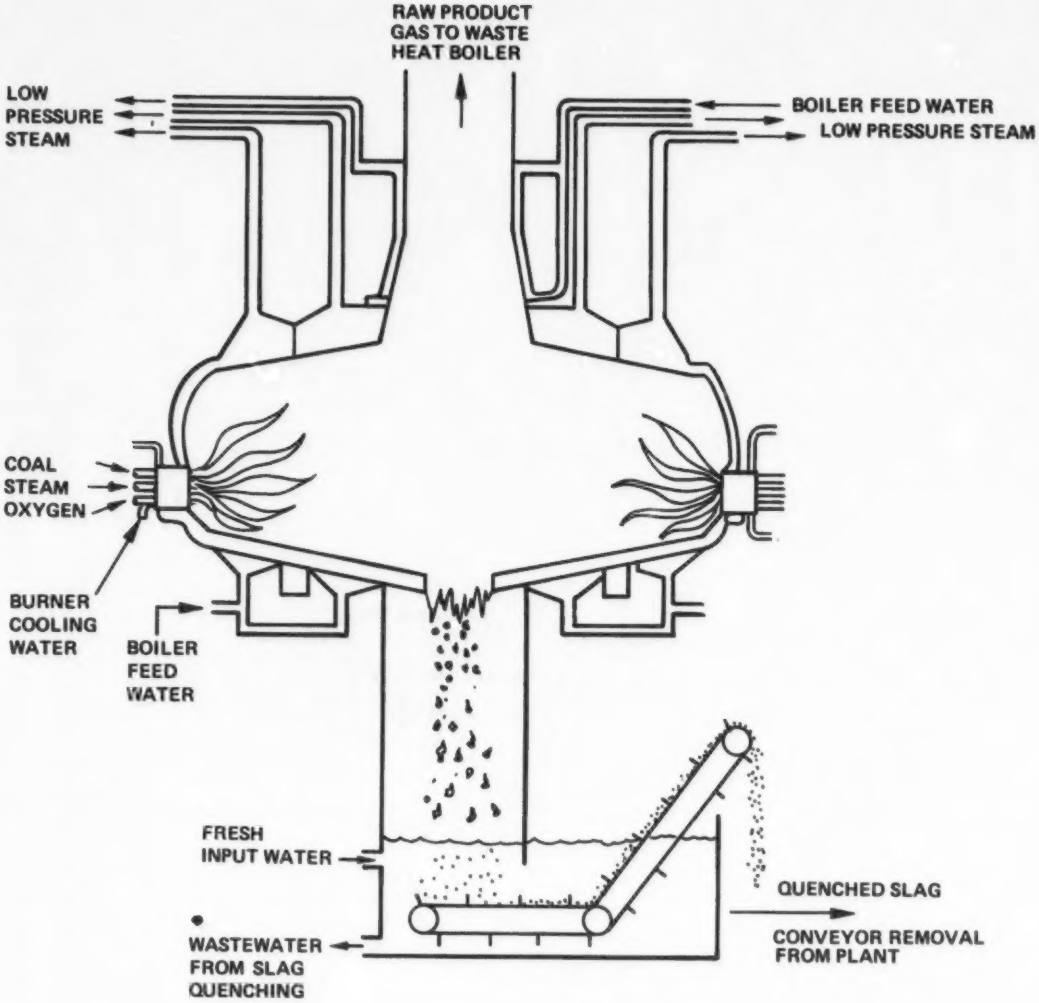
RAW PRODUCT GAS TO WASTE HEAT BOILER
LOW PRESSURE STEAM
BOILER FEED WATER
LOW PRESSURE STEAM
COAL
STEAM
OXYGEN
BURNER COOLING WATER
BOILER FEED WATER
FRESH INPUT WATER
WASTEWATER FROM SLAG QUENCHING
QUENCHED SLAG
CONVEYOR REMOVAL FROM PLANT

Figure 1. Koppers-Totzek Gasifier

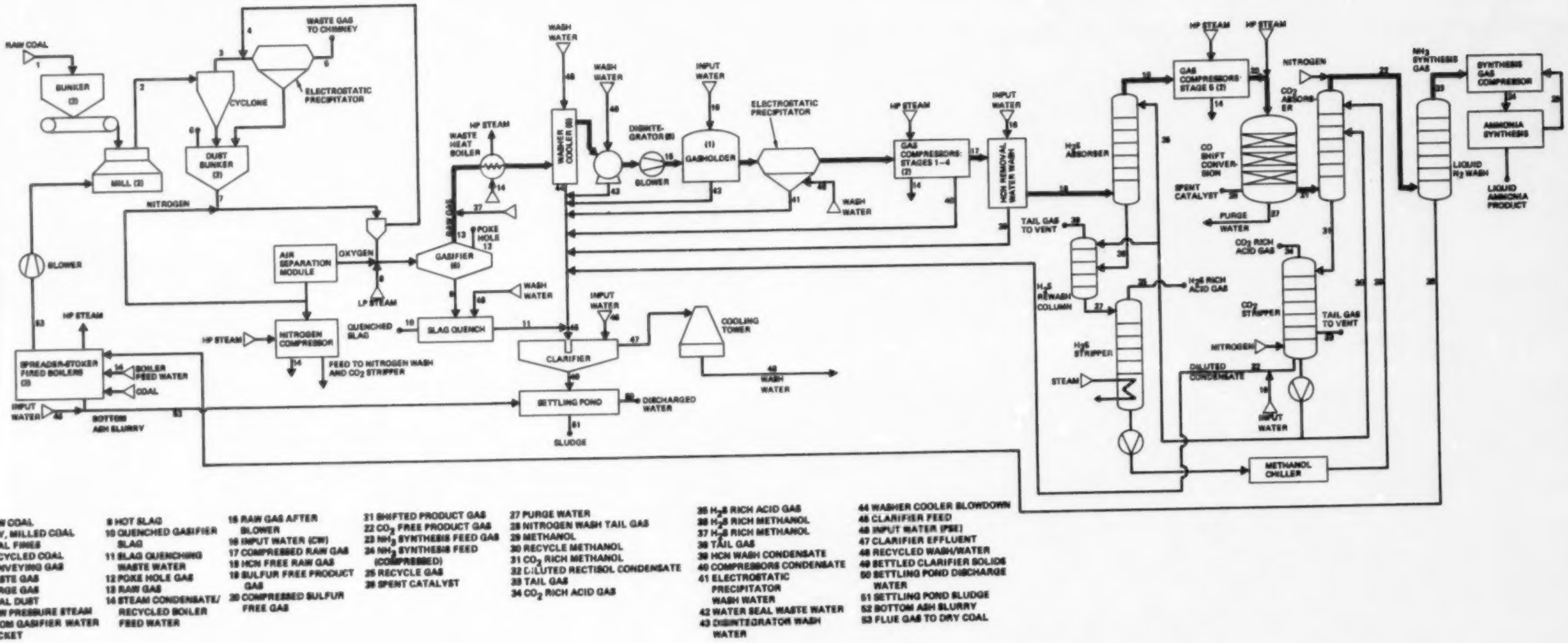
RAW COAL
BUNKER (2)
MILL (2)
CYCLONE
ELECTROSTATIC PRECIPITATOR
WASTE GAS TO CHIMNEY
DUST BUNKER (2)
NITROGEN
AIR SEPARATION MODULE
OXYGEN
LP STEAM
NITROGEN COMPRESSOR
HP STEAM
FEED TO NITROGEN WASH AND CO2 STRIPPER
BLOWER
SPREADER-STOKER FIRED BOILERS (3)
BOILER FEED WATER
COAL
INPUT WATER
BOTTOM ASH SLURRY
GASIFIER (6)
POKE HOLE
RAW GAS
QUENCHED SLAG
SLAG QUENCH
WASH WATER
WASTE HEAT BOILER
WASHER COOLER (6)
DISINTEGRATOR (6)
BLOWER
INPUT WATER
GASHOLDER (1)
ELECTROSTATIC PRECIPITATOR
CLARIFIER
COOLING TOWER
SETTLING POND
DISCHARGED WATER
SLUDGE
GAS COMPRESSORS: STAGES 1–4 (2)
HCN REMOVAL WATER WASH
H2S ABSORBER
TAIL GAS TO VENT
H2S REWASH COLUMN
H2S STRIPPER
STEAM
H2S RICH ACID GAS
GAS COMPRESSORS: STAGE 5 (2)
CO SHIFT CONVERSION
SPENT CATALYST
PURGE WATER
CO2 ABSORBER
CO2 RICH ACID GAS
CO2 STRIPPER
TAIL GAS TO VENT
NITROGEN
DILUTED CONDENSATE
METHANOL CHILLER
NH3 SYNTHESIS GAS
LIQUID N2 WASH
SYNTHESIS GAS COMPRESSOR
AMMONIA SYNTHESIS
LIQUID AMMONIA PRODUCT
1 RAW COAL
2 DRY, MILLED COAL
3 COAL FINES
4 RECYCLED COAL CONVEYING GAS
5 WASTE GAS
6 PURGE GAS
7 COAL DUST
8 LOW PRESSURE STEAM FROM GASIFIER WATER JACKET
9 HOT SLAG
10 QUENCHED GASIFIER SLAG
11 SLAG QUENCHING WASTE WATER
12 POKE HOLE GAS
13 RAW GAS
14 STEAM CONDENSATE/ RECYCLED BOILER FEED WATER
15 RAW GAS AFTER BLOWER
16 INPUT WATER (CW)
17 COMPRESSED RAW GAS
18 HCN FREE RAW GAS
19 SULFUR FREE PRODUCT GAS
20 COMPRESSED SULFUR FREE GAS
21 SHIFTED PRODUCT GAS
22 CO2 FREE PRODUCT GAS
23 NH3 SYNTHESIS FEED GAS
24 NH3 SYNTHESIS FEED (COMPRESSED)
25 RECYCLE GAS
26 SPENT CATALYST
27 PURGE WATER
28 NITROGEN WASH TAIL GAS
29 METHANOL
30 RECYCLE METHANOL
31 CO2 RICH METHANOL
32 DILUTED RECTISOL CONDENSATE
33 TAIL GAS
34 CO2 RICH ACID GAS
35 H2S RICH ACID GAS
36 H2S RICH METHANOL
37 H2S RICH METHANOL
38 TAIL GAS
39 HCN WASH CONDENSATE
40 COMPRESSORS CONDENSATE
41 ELECTROSTATIC PRECIPITATOR WASH WATER
42 WATER SEAL WASTE WATER
43 DISINTEGRATOR WASH WATER
44 WASHER COOLER BLOWDOWN
45 CLARIFIER FEED
46 INPUT WATER (PSE)
47 CLARIFIER EFFLUENT
48 RECYCLED WASH/WATER
49 SETTLED CLARIFIER SOLIDS
50 SETTLING POND DISCHARGE WATER
51 SETTLING POND SLUDGE
52 BOTTOM ASH SLURRY
53 FLUE GAS TO DRY COAL

Figure 2. Diagram of Number 4 Ammonia Plant at Modderfontein

APPROACH

The nine streams included in this STE along with their stream numbers which correspond to Figure 2, are as follows:

- Solids
    - Coal Dust Feed/7
- Gas Streams
    - Raw Product Gas/15
    - Tail Gas from H_2S Absorber/38
    - Tail Gas from CO_2 Absorber/33
- Aqueous Streams
    - Input Water (Purified Sewage Effluent)/46
    - Input Water (Cooling Water)/16
    - Settling Pond Effluent/50
    - Compressor Condensate Wastewater/40
    - Diluted Rectisol Condensate Wastewater/32

The basic approach was to perform a comprehensive organic and inorganic characterization of these nine streams per the EPA procedures for Level 1 and Level 2 environmental assessments and for Priority Pollutants (1, 2, 3). The Level 1 methods provide a broad semi-quantitative survey from which constituents found to be present at levels of potential concern are selected for further quantitative examination, Level 2. The Priority Pollutant screening consists of analyses for a specific list of 129 pollutants of concern to the EPA.

The sampling and analysis responsibilities for the K-T facility test were divided between TRW and GKT. GKT performed all of the sampling and most of the on-site analyses during a three week period in November 1979. TRW arranged to have the remaining time-critical analyses performed by a local South African laboratory (McLachlan & Lazar pty LTD) and to have portions of the coal feed and aqueous process stream samples shipped back to TRW for analysis.

Level 1 Analysis

Most of the Level 1 analyses that are time critical were performed by GKT (i.e., all gas analyses and most wastewater quality tests). The only wastewater quality tests remaining were nitrates and BOD, which were then handled by McLachlan & Lazar in Johannesburg. Replicate analysis of a few of the species measured by GKT were also performed by the local lab for quality assurance. The methods used by GKT and the commercial laboratory were for the most part comparable to U.S. methods and were acceptable for source evaluations. The analysis of organic materials and trace metals was performed by TRW on preserved aliquots of the aqueous stream samples that were shipped back to the U.S. The methods used for the Level 1 analyses were taken from the EPA-IERL/RTP procedures manual (1).

Level 2 Analysis

Level 2 analyses of the aqueous Modderfontein samples consisted of atomic absorption techniques (AAS) for Fe and Mn, and a high performance liquid chromatography (HPLC) technique for polynuclear organic material (POM) compounds. These two metals and the POM compounds were selected on the basis of comparing the Level 1 data to the EPA's discharge multimedia environmental goal values (4), thus determining the potentially hazardous species present which warranted further investigation, and by examining which Level 2 data requirements had not already been met by either the wastewater quality or priority pollutant analyses.

The AAS techniques were standard methods (5). The HPLC technique for POMs utilized a reverse phase, quarternary solvent system for separation of three-ring and larger POM compounds. Both UV and fluorescence detectors were used in tandem in order to yield corroborative data for the identification and quantitation of the compounds present. Further qualitative data for POM identification was obtained by collecting the HPLC fractions and analyzing them by GC/MS.

Priority Pollutant Screening Analysis

The analyses for organic priority pollutants were done in three phases. Volatile, acid extractable non-volatile and base-neutral extractable non-volatile organics were tested in accordance with the EPA procedures manual (3). The samples were analyzed by computerized gas chromatography-mass spectrometry (GC/MS) using an INCOS data system. A computer program was used to reduce the data. The results were manually examined and if necessary, modified. The thirteen priority pollutant metals (i.e., Ag, As, Be, Cd, Cr, Cu, Hg, Pb, Mn, Sb, Se, Tl, and Zn) were analyzed by a combination of flame and flameless atomic absorption techniques in accordance with the EPA protocol (3).

Source Analysis Model

All of the data obtained from this STE were used in the EPA's Source Analysis Model/IA, which compares the measured concentrations of the constituents analyzed to the EPA's Discharge Multimedia Environmental Goals (6). This model calculates discharge severities based on the constituent concentrations alone (total discharge severity) and on the concentrations combined with the stream flow rate (weighted discharge severity). This approach is being used uniformly by all of the EPA's contractors in the coal conversion area and thus provides a consistent basis for evaluating STE data.

RESULTS

Coal Feed Stream

The results of the proximate and ultimate analysis on the coal feed, shown in Table 1, show that the sample may be characterized as Bituminous, High Volatile B coal. When compared to must U.S. coals it is found to be very high in ash content and low in sulfur. A trace element survey, more precise determinations of the major minerals present and other measurements were also performed. This data will be included in the Source Test and Evaluation Report currently in preparation for the EPA.

Gas Streams

All gas analyses were performed by GKT and the data obtained are shown in Table 2. The raw gas results reflect the average composition from all five gasifiers (the stream was sampled at a common line leading to the gas holder) after the gas has been water-washed for particulate removal. A description of the major reactions that take place in the raw gas washing stages is as follows:

- NH_3, HCN, SO_2, and to a small degree H_2S and CO_2, are dissolved in the wash water.
- H_2S is eventually converted to $S_2O_3^{=}$, $SO_4^{=}$, and insoluble metal sulfides due to the pH, temperature, and flyash content of the water.
- HCN reacts with the sulfur compounds to form SCN^- and with the iron content of the flyash to form insoluble complexes.
- Additional oxidation reactions occur which are catalyzed by the flyash involving NH_3, $SO_3^{=}$, $S_2O_3^{=}$, CN^-, and SCN^-.

TABLE 1

PROXIMATE AND ULTIMATE RESULTS FROM COAL ANALYSIS

Proximate Analysis	As Received
% Moisture	1.49
% Ash	19.60
% Volatile	27.52
% Fixed Carbon	51.39
	100.00
Btu/lb.	10853
% Sulfur	0.99

Ultimate Analysis	As Received
% Moisture	1.49
% Carbon	64.41
% Hydrogen	3.72
% Nitrogen	1.12
% Chlorine	0.01
% Sulfur	0.99
% Ash	19.60
% Oxygen (diff)	8.66
	100.00

Table 2. GAS ANALYSIS DATA

Parameter/Units	Raw Gas	Tail Gas from H_2S Rewash Column	Tail Gas from CO_2 Stripper
Flowrate, Nm^3/hr	103,600	13,700	48,800
H_2O g/Nm^3	54	5	5
H_2 Vol.% (dry)	28.2	<0.1	<0.1
CO "	59.1	1.9	0.3
CO_2 "	10.9	52.6	84.3
N_2/Ar* "	1.8	45.5	15.4
CH_4 "	<0.1	<0.1	<0.1
H_2S mg/Nm^3 (dry)	6,300	†	<1
COS "	740	†	<3
CS_2 "	450	†	<10
SO_2 "	14	<3	<3
NH_3 "	57	39	3
HCN "	76	62	8
NO_X "	28	<1	<1
Mercaptans "	<1	<1	<1

* By difference

† Not determined

The main components in the water-washed gas are then H_2O, CO, CO_2, H_2, and N_2. Data on hydrocarbons contained in the raw gas stream were not obtained due to problems with on-site analytical instrumentation, but low concentrations would be expected due to the high temperature of the K-T gasification reaction.

The two tail gas streams from the Rectisol module consist primarily of CO_2, the nitrogen used for methanol stripping, small amounts of CO and H_2O and traces of NH_3 and HCN. During the test period, plant operating data indicated that temperature control in the Rectisol unit was not working properly with the result that sulfur species levels in the H_2S stripper tail gas were outside design specifications and were not typical of normal Rectisol unit operation. Therefore sulfur species data on this tail gas stream are not included in Table 2. A design value of less than 2 ppm total sulfur is quoted by GKT.

Use of the SAM/IA model, which assesses the potential health and ecological effects of discharge streams based on chemical constituents, yielded the calculated Total Discharge Severity (TDS) and Weighted Discharge Severity (WDS) values shown in Table 3. In the tail gas stream from the H_2S absorber, CO, HCN, and NH_3 are present at levels of potential concern; and in the tail gas from the CO_2 absorber, CO and NH_3 are of concern.

Table 3. SUMMARY OF SAM/IA TDS AND WDS RESULTS FOR GAS STREAMS

TDS and WDS Values	Tail Gas from H_2S Rewash	Tail Gas from CO_2 Stripper
Total Discharge Severity (TDS)		
Health-Based	5.6 E + 02	7.6 E + 01
Ecology-Based	2.9 E + 02	3.4 E + 01
Weighted Discharge Severity (WDS)		
Health-Based	2.1 E + 03	1.0 E + 03
Ecology-Based	1.1 E + 03	4.6 E + 02

Aqueous Streams

The results of the Level 1 standard wastewater analyses performed jointly by GKT, TRW and McLachlan & Lazar are summarized in Table 4. The

Table 4. WASTEWATER QUALITY TEST DATA

Parameter/Units	Input Water (PSE)	Input Water (CW)	Settling Pond Effluent	Process Waters	
				Compressor Condensate	Rectisol Condensate
Flowrate, m^3/hr	215	34	230	9.1	3.9
pH	6.8	8.5	8.7	8.1	8.6
TSS, mg/L	<1	8	<1	6	45
TDS,mg/L	1,580	1,460	1,560	220	1,520
Hardness, mg/L	450	620	540	53	620
Conductivity,µmhos/cm	2,300	1,900	2,100	5,800	1,900
BOD, mg/L	5	4	4	550	800
COD, mg/L	16	24	4	600	1,600
TOC, mg/L	31	16	5	140	590
NH_3, mg/L	73	3	33	940	38
CN^-, mg/L	0.2	1.2	0.2	8.9	2.8
SCN^-, mg/L	2.1	2.1	1.8	14	120
H_2S, mg/L	<1	<1	<1	49	2.8
$S_2O_3^=$, mg/L	<1	<1	<1	6.3	17
$SO_3^=$, mg/L	<1	<1	<1	<1	<1
$SO_4^=$, mg/L	580	850	730	53	500

settling pond effluent, the only aqueous stream discharged by the plant, appears from the data to be quite similar to the input waters. This would seem to indicate that any aqueous pollutants contributed by the gasification process are esentially removed in the settling pond.

The results of the Level 1 survey for organics, shown in Table 5, indicate that the total organic loading was low and that the material present was primarily nonvolatile (BP >100°C). Examination of the nonvolatile material by infrared (IR) spectroscopy indicated that the classes of compounds present in all of the samples are primarily saturated hydrocarbons along with some esters. There was also some IR evidence of low levels of aromatic hydrocarbons present in the compressor condensate and Rectisol unit samples. Examination of the nonvolatile samples by solids probe low resolution mass spectroscopy (LRMS) yielded additional information regarding the classes of compounds present. The intensity of the mass spectra peaks were used to assign relative concentration factors (100 = major, 10 = minor, 1 = trace) to the compound classes identified. The LRMS results are summarized in Table 6. The mass spectra data confirm the IR data indicating the presence of aliphatic hydrocarbons, esters, and traces of aromatics. Traces of phenols, cresols, and alcohols also appear in many of the samples. Significant levels of elemental sulfur (S_8) are also seen because of its appreciable solubility in the solvent used for these extractions (methylene chloride).

Table 5. LEVEL 1 ORGANIC SURVEY DATA

Stream/Flowrate	Volatiles (mg/L)	Non-Volatiles (mg/L)	Total Organics (mg/L)
Input Water (PSE)/215 m^3/hr	0.04	0.68	0.72
Input Water (CW)/34 m^3/hr	<0.01	0.88	0.88
Settling Pond Effluent/230 m^3/hr	0.05	0.06	0.10
Process Streams			
Compressor Condensate/9.1 m^3/hr	0.01	3.83	3.84
Rectisol Condensate/3.9 m^3/hr	0.49	33.4	33.9

Table 6. ORGANIC COMPOUND CLASS DATA

Stream	Compound Class	Contribution to Total Organics
Input Water (PSE)	Esters (phthalates)	Major
	Nitro Aromatic Hydrocarbons	Minor
	Primary Alcohols	Minor
Input Water (CW)	Esters (phthalates)	Major
Settling Pond Effluent	Primary Alcohols	Major
	Secondary Alcohols	Major
	Aliphatic Hydrocarbons	Minor
	Esters (phthalates)	Minor
	Unsaturated Alkyl Halides	Trace
	Ketones	Trace
Process Streams		
Compressor Condensate	Sulfur (S_8)	Major
	Ethers	Major
	Esters (phthalates)	Minor
	Phenols	Trace
	Chlorinated Phenols	Trace
	Chlorinated Cresols	Trace
	Polynuclear Organic Materials (POMs)	Trace
	Carboxylic Acids	Trace
Rectisol Condensate	Aliphatic Hydrocarbons	Major
	Sulfur (S_8)	Minor
	Polynuclear Organic Materials (POMs)	Trace
	Phenols	Trace
	Esters (phthalates)	Trace

The Level 1 inorganic survey of the aqueous samples consisted of a spark source mass spectroscopy (SSMS) analysis. The data indicated that, based upon elemental composition, the settling pond effluent is quite similar to the input waters. Similarity between these streams based upon standard wastewater parameters was previously noted. The only trace elements that show an increase from input water levels to settling pond effluent levels are cesium, strontium, barium, gallium, and molybdenum. This is in general agreement with the trace element analysis of the coal. Other elements (i.e., aluminum, iron, and manganese) actually show a significant decrease in the settling pond effluent compared to the input water.

As is mentioned in the analytical approach, the Level 1 data were compared to the EPA's Discharge Multimedia Environmental Goals (DMEGs) using the SAM/IA model in order to determine which species were present at levels of potential concern and were thus candidates for further investigation. Those species determined to be of interest were then compared to the priority pollutant list. It was found that most of the Level 2 data requirements would be satisfied by the priority pollutant analyses and that the only additional determinations needed were the quantitation of Fe and Mn in most of the samples and quantitation of polynuclear organic material (POM) compounds in the Rectisol condensate samples. It is thus appropriate to discuss the Level 2 and priority pollutant results together as a coordinated analytical effort.

The organic priority pollutant data are summarized in Table 7. The results show that very few of the 116 organic priority pollutant compounds were found. Those that were present were mostly at very low concentrations. The level of concern specified by the EPA's Effluent Guidelines Division is 10 μg/L.

The results of the HPLC analysis for POMs performed on the methylene chloride extracts from the two Rectisol unit samples indicated that each extract contained essentially the same POMs at very similar levels. Eleven distinct POM compounds were detected. Comparison of retention time data as well as relative response ratio for the two detectors with similar data for available standards enabled the positive identification and quantitation of five compounds, Table 8. Those compounds which overlap

Table 7. ORGANIC PRIORITY POLLUTANT DATA

Sampling Day	Stream Description/Stream Number	Priority Pollutant Compounds Found					
		Base/Neutral Fraction		Acid Fraction		Volatiles	
		Compound	µg/L	Compound	µg/L	Compound	µg/L
Nov. 12	Input Water--Purified Sewage Effluent	Nitrobenzene 1,2,4-Trichlorobenzene Isophorone Bis (2-Ethylhexyl)phthalate Di-n-octylphthalate	T T T T T	None Detected		None Detected	
Nov. 19	Input Water--Cooling Water	Butylbenzylphthalate	T	None Detected		Chloroform	T
Nov. 12	Settling Pond Effluent	None Detected		None Detected		None Detected	
Nov. 19	Settling Pond Effluent	Butylbenzylphthalate	T	None Detected		Chloroform	T
Nov. 12	Combined Condensates from #1--4 Compressors	Naphthalene	T	4-Chloro-m-Cresol	2.3	None Detected	
Nov. 19	Combined Condensates from #1--4 Compressors	Naphthalene Diethylphthalate Di-n-butylphthalate Butylbenzylphthalate	T T 6.0 T	Phenol Pentachlorophenol	T T	Chloromethane Bromomethane Chloroform	7.8 49 T
Nov. 12	Condensate from Rectisol Unit	Naphthalene Fluorene Anthracene plus phenanthrene Fluoranthene Pyrene Butylbenzylphthalate	T T T 6.3 25 T	None Detected		Chloroform	T
Nov. 19	Condensate from Rectisol Unit	Acenaphthalene Dimethylphthalate Fluorene Diethylphthalate Anthracene plus phenanthrene Fluoranthene Pyrene Chrysene	T T 1.0 T 4.6 19 97 34	Phenol 2,4-Dimethylphenol	T T	Chloroform	T

T = Trace (<1µg/L)

Table 8. LEVEL 2 POM DATA

Compounds Identified	11/12/79 Rectisol Condensate	11/19/79 Rectisol Condensate
Fluoranthene	24 μg/L	17 μg/L
Pyrene	32 μg/L	25 μg/L
1,2-Benzofluorene	15 μg/L	15 μg/L
1,2-Benzanthracene	23 μg/L	16 μg/L
Benzo(k)fluoranthene	2 μg/L	2 μg/L

with the priority pollutant screening (i.e., fluoranthene and pyrene) are more accurately quantitated by the HPLC technique. The priority pollutant screening also identified a four-ringed compound as chrysene which in the HPLC analysis was determined to be 1,2-benzanthracene (also four-ringed).

HPLC fractions were collected and analyzed by gas chromatography/mass spectrometry (GC/MS) to obtain molecular weight data on the remaining unknown compounds. The five unidentified POMs are believed to be present at levels less than 30 μg/L based on the HPLC peak areas. They had molecular weights of 230 (1), 242 (2), and 252 (2).

The health-based DMEGs for the identified POM compounds range from 670 μg/L to 24,000 μg/L, while ecology-based DMEGs are 100 μg/L for all five of these POMS. Comparison of data and DMEGs shows that the levels measured would not be considered to be of concern.

It should be noted that the very toxic POM benzo(a)pyrene was one of the standards used in this analysis. None of the HPLC peaks matched the retention time and response ratios for B(a)P. Thus the unidentified compounds with MW 252 are clearly some other POM with the identical molecular weight.

The priority pollutant metals screening involves the analysis of 13 elements each of which has its own level of concern. These elements and the corresponding levels of concern which have been defined by the EPA are: Ag - 5 ppb, Tl - 50 ppb, Sb - 100 ppb, As - 25 ppb, Se - 10 ppb, Zn - 1,000 ppb, Pb - 25 ppb, Cd - 5 ppb, Ni - 500 ppb, Be - 50 ppb, Cu - 20 ppb, Cr - 25 ppb, and Hg - 1 ppb. The results obtained from atomic adsorption and emission spectroscopy analyses for these thirteen elements plus the two elements (Fe and Mn) quantitated for Level 2 requirements are presented in Table 9. The data show that the process waters (compressor condensate and Rectisol unit samples) frequently exceed the levels of concern particularly for Se, Zn, Cu and Hg. However, as was noticed in the Level 1 SSMS inorganic survey, the only aqueous discharged stream (settling pond effluent) is relatively clean compared to both the process streams and the input waters (purified sewage effluent and cooling water). Overall reduction in trace element levels across the plant were observed for Sb, As, Zn, Pb, Ni and Ca.

All of the data obtained on the aqueous streams were evaluated using the SAM/IA model to assess the potential health and ecological effects of the streams. Of particular interest is the discharged stream, the settling pond effluent. The TDS and WDS values obtained for this discharge as compared to the input streams supplied as process water to the plant, are summarized in Table 10. The fact that the health-based values for the aqueous input and discharge streams reflect a potential concern is due mainly to Mn and Fe and to a lesser extent phosphorus. The ecology-based values are entirely due to phosphorus. The ecology DMEG value for phosphorus and its various anions is extremely low (0.5 μg/L) and thus easily becomes the most significant value obtained in the SAM/IA calculations. However ecology-based severity values >1 were also obtained for Cd, Cu, Mn, Ni, Pb, S, Zn, and phthalate esters in the input water streams and Cd, Mn, Ni, and S in the settling pond discharge stream. The reduction in both TDS and WDS values for the effluent versus the input water appears to be due to a decrease in the concentrations of the phthalate esters, phosphorus, Cu, Pb, and Zn. These and other constituents as well appear to be transferred to the settling pond sludge.

Table 9. INORGANIC PRIORITY POLLUTANT AND LEVEL 2 DATA

Element	Concentration, ppb				
	Input Water (PSE)	Input Water (CW)	Settling Pond Effluent	Process Waters	
				Compressor Condensate	Rectisol Condensate
Antimony	10	<3	<3	<3	<3
Arsenic	33	<5	9	<5	11
Beryllium	<0.5	<0.5	<0.5	<0.5	<0.5
Cadmium	1.3	<0.5	<0.5	<0.5	<0.5
Chromium	<5	7	6	6	7
Copper	78	43	6	31	90
Lead	50	28	<5	19	13
Mercury	0.5	<0.2	<0.2	250	23
Nickel	180	<10	<10	<10	190
Selenium	<2	<2	3	3,500	26
Silver	<1	<1	<1	<1	<1
Thallium	<5	<5	<5	<5	<5
Zinc	660	3,500	<100	270	2,600
Iron	<100	700	140	1,200	4,000
Manganese	1,300	<50	720	<25	50

Table 10. SAM/IA RESULTS FOR AQUEOUS STREAMS

Stream	Total Discharge Severity (TDS)		Weighted Discharge Severity (WDS)	
	Health-Based	Ecology-Based	Health-Based	Ecology-Based
Discharge Water--Settling Pond Effluent	6.1 E + 00	1.9 E + 02	3.9 E + 02	1.2 E + 04
Input Water--Purified Treated Sewage	9.8 E + 00	1.6 E + 04	5.9 E + 02	9.6 E + 05
Input Water--Cooling Water	6.7 E + 00	4.2 E + 03	6.4 E + 01	4.0 E + 04

CONCLUSIONS

The limited source test program conducted at the Modderfontein facility has provided some of the key data needed for the environmental assessment of Koppers-Totzek based synthetic fuels plant which may be built in the United States. The data obtained do not indicate that any special problems should be encountered in controlling the process effluents to environmentally acceptable levels for plants built in the U.S. For example, the wastewater treatment at Modderfontein, consisting of a clarifier and settling pond, was adequate to produce a final discharge that had lower pollutant levels than the fresh input waters supplied to the plant.

Relatively steady state conditions were realized during the test period, thus most of the samples taken were generally representative of typical plant operation. This in turn indicates that the data can reliably be used as intended. Nearly full design capacity was obtained throughout the test period. All collection of samples and associated operating data occurred at production rates of between 102,000 and 104,000 normal cubic meters per hour (Nm^3/h) of dry raw gas and the gasification plant operated in a very stable manner with no process upsets.

ACKNOWLEDGMENTS

TRW wishes to acknowledge GKT Gesellschaft für Kohle-Technologie mbH for their interest and willingness to participate in this effort thus making the field tests possible. Some of the key individuals from GKT were Mr. Herbert Stempelmann, Dr. Gerhard Preusser, and Dr. B. Firnhaber. The cooperation of AECI Limited in allowing their plant to be tested is also gratefully acknowledged. Further acknowledgment goes to Mr. Robin Lazar and the Staff of McLachlan & Lazar (pty) LTD, for their assistance in the analysis, preservation, and shipment of samples for TRW. TRW also acknowledges the assistance and guidance of their EPA Project Officer, Mr. William J. Rhodes.

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AN ENVIRONMENTALLY BASED EVALUATION OF THE MULTIMEDIA DISCHARGES FROM THE KOSOVO LURGI COAL GASIFICATION SYSTEM

By

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ABSTRACT

The U.S. Environmental Protection Agency and the government of Yugoslavia have jointly sponsored a cooperative environmental data acquisition program. This program has focused upon a commercial-scale medium-Btu Lurgi gasification facility which is currently operating in the Kosovo region of Yugoslavia. The objective of this program was to characterize the uncontrolled discharge streams associated with the Kosovo facility in order to gain insight into control technology needs for future U.S. Lurgi plants. The Kosovo study was undertaken because the Lurgi process has a significant potential for future use in the United States.

In the Kosovo test program, the most environmentally significant components in the plant's key feed, product, and discharge streams were identified and quantified. Also, selected in-plant process streams were sampled and analyzed to gain insight into how specific pollutants distributed themselves among the plant's gaseous, aqueous, and solid discharge streams. The EPA's Source Analysis Model/1A was used to identify and prioritize the pollutants found in the plant's discharge streams.

The results of the Kosovo test program indicate that there are many gaseous, aqueous, and solid discharge streams from a Lurgi gasification facility which have the potential to significantly impact the environment. The key pollutants identified in the plant's gaseous discharge streams included reduced sulfur and nitrogen species (H_2S, mercaptans, HCN, and ammonia), hydrocarbons (benzene), and CO. Key pollutants in the Phenosolvan wastewater included phenols, cyanides, sulfides, and total organics. Effective controls for the waste streams containing these pollutants will be essential to minimize the environmental problems associated with Lurgi gasification technology.

In general, trace elements were not found to be a significant problem at Kosovo. The dry gasifier ash met the RCRA Extraction Procedure test criteria for nonhazardous wastes. Trace organics, particularly polynuclear aromatic compounds which are likely to be present in streams containing tar aerosols, should be given attention in the development of controls for U.S. Lurgi facilities.

AN ENVIRONMENTALLY BASED EVALUATION OF THE MULTIMEDIA DISCHARGES FROM THE KOSOVO LURGI COAL GASIFICATION SYSTEM

An international program sponsored by the Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency, is being conducted in the Kosovo region of Yugoslavia to characterize potential environmental problems associated with Lurgi gasification technology. The study, conducted over a three year period, was a cooperative endeavor between scientists from Yugoslavia and EPA/Radian. The program was undertaken because the Lurgi gasification process has significant potential for use in the United States.

The purpose of the Kosovo study was to characterize the uncontrolled discharges from a commercial Lurgi facility. This was done to gain insight into the environmental control needs for future U.S. Lurgi gasification plants. The test program was conducted in four phases whose objectives were:

Phase	Objective
I	Identify and quantify major and minor pollutants in the plant's discharge streams.
II	Identify and quantify trace pollutants in the plant's discharge streams.
III	Characterize ambient air pollutants in the plant's vicinity.
IV	Measure fugitive emission rates in the plant.

The program schedule is shown in Figure 1. Negotiations for this cooperative program were initiated in 1974. Testing, which was initiated in 1977, has been carried out in six individual campaigns over a three year period. Phase I results were reported previously (Ref. 1 through 3). Documentation of the results from Phases II and III will become available in 1981. Testing for fugitive emissions (Phase IV) was completed in August, 1980, and the results are currently being evaluated.

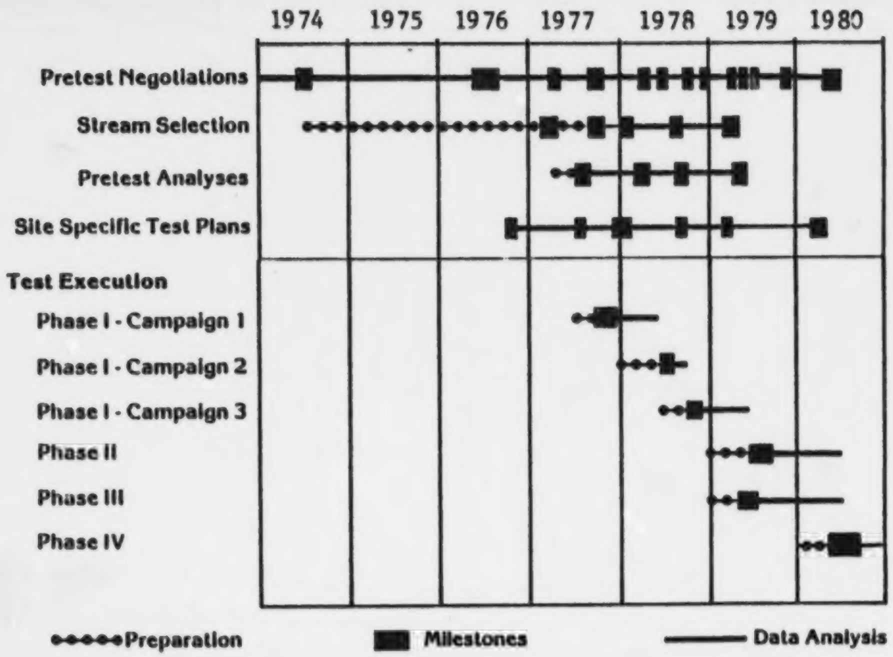


Figure 1. Kosovo test program schedule.

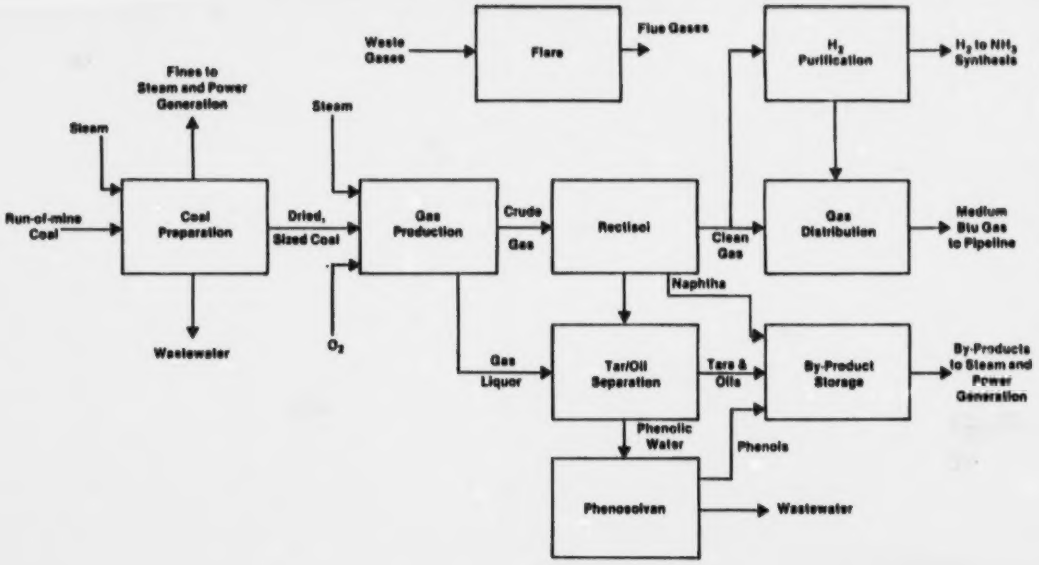

Waste Gases
Flare
Flue Gases
H_2 Purification
H_2 to NH_3 Synthesis
Fines to Steam and Power Generation
Steam
Steam
Run-of-mine Coal
Coal Preparation
Dried, Sized Coal
Gas Production
Crude Gas
Rectisol
Clean Gas
Gas Distribution
Medium Btu Gas to Pipeline
Wastewater
O_2
Naphtha
Gas Liquor
Tar/Oil Separation
Tars & Oils
By-Product Storage
By-Products to Steam and Power Generation
Phenolic Water
Phenols
Phenosolvan
Wastewater

Figure 2. Simplified flow diagram of the Kosovo coal gasification plant.

This paper presents an overview of the Phase I and II test results. These results address the major, minor, and trace pollutants found in the plant's key process and discharge streams. An assessment of the severity of the plant's gaseous, aqueous, and solid discharges is included. This assessment is based upon the use of the EPA-IERL's Source Analysis Model/1A (SAM/1A). This model prioritizes pollutants based on their potential for causing adverse health effects.

Plant Description

Detailed descriptions of the Kosovo coal gasification plant were provided in previous publications (Ref. 1 through 3). A brief plant description is included here to facilitate understanding of the results.

The Kosovo Lurgi gasification facility is an integral part of a large mine-mouth industrial complex. A simplified flow diagram is shown in Figure 2. The gasification plant consumes dried lignite and produces two primary products: a medium-Btu fuel gas having a net heating value of approximately 14 MJ/m^3 @ 25°C (360 Btu/scf), and hydrogen which is used as an ammonia synthesis feedstock. Several hydrocarbon by-products including light tar, medium oil, naphtha, and crude phenol are also produced.

Run-of-mine coal which contains around 50 weight percent moisture is dried by the Fleissner process (high temperature steam soak) to around 25 weight percent moisture and sized to select particles between 6 and 60 mm in diameter. Typical feed coal properties are presented in the results section. After sizing, the dried coal is fed to the Lurgi gasifiers where it reacts with oxygen and steam at 2.5 MPa (25 atm) pressure. The crude product gas is cooled and then cleaned to remove acid gases prior to its transportation by pipeline to the utilization site. In the cooling step, tars, oils, naphtha, and phenolic water are condensed and removed from the gas. In the acid gas removal step, H_2S and CO_2 are removed by sorption into cold methanol. The rich methanol is regenerated by depressurization and heating. The H_2S-rich waste gas released by the regeneration step is sent to a flare while the CO_2-rich waste gas is vented directly to the atmosphere. Tar and oil are separated from the phenolic water by decantation after which the water soluble organics (crude phenols) are removed from the wastewater by extraction with diisopropyl ether. Four liquid by-products: naphtha, medium oil, light tar, and crude phenol are collected in storage tanks and used as fuels. Ammonia, removed from the phenolic water by steam stripping, is vented to the atmosphere.

Figure 3 shows the design flow rates of the plant's major inlet and outlet streams. These flow rates are based on design conditions with five of six Lurgi gasifiers in operation. As indicated in Figure 3, the plant is designed to produce 25 Mg (65,000 m^3 @ 25°C) of product gas for every 80 Mg of dried coal consumed.

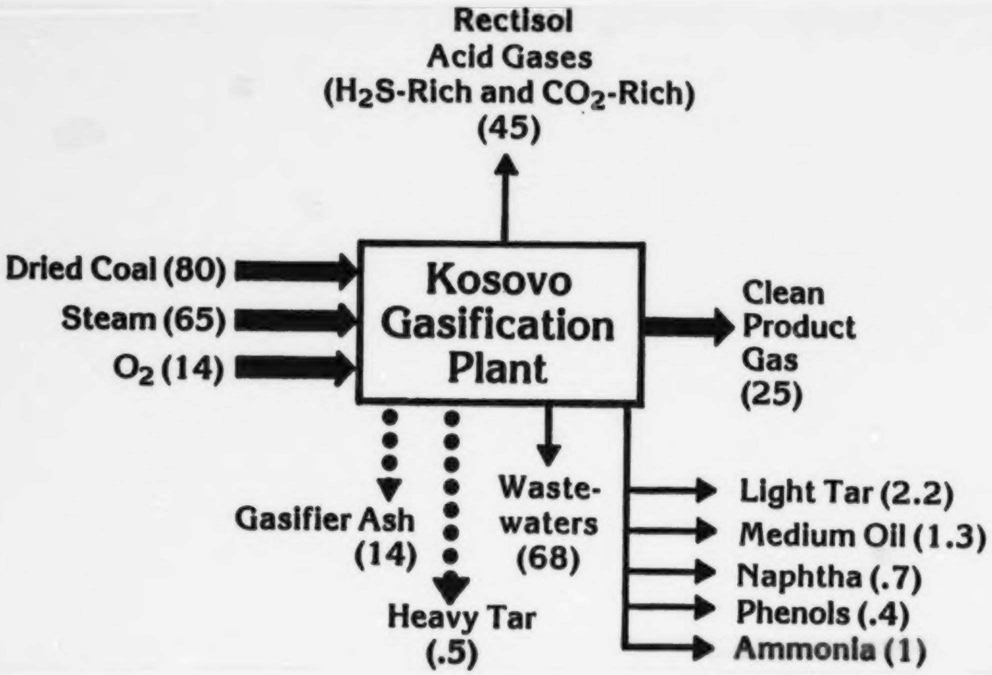
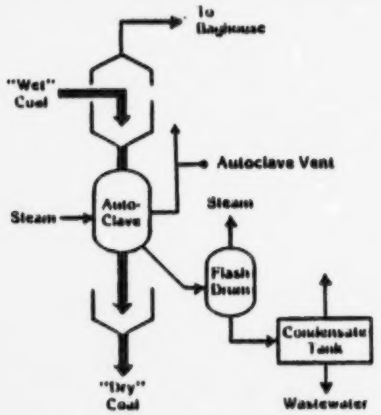

Rectisol
Acid Gases
(H_2S-Rich and CO_2-Rich)
(45)
Dried Coal (80)
Steam (65)
O_2 (14)
Kosovo Gasification Plant
Clean Product Gas (25)
Gasifier Ash (14)
Heavy Tar (.5)
Waste-waters (68)
Light Tar (2.2)
Medium Oil (1.3)
Naphtha (.7)
Phenols (.4)
Ammonia (1)

Figure 3. Major stream flow rates in the Kosovo gasification plant (megagrams/hr).


To Baghouse
"Wet" Coal
Autoclave Vent
Steam
Auto-Clave
Steam
Flash Drum
Condensate Tank
"Dry" Coal
Wastewater

——● - indicates sampling point

Figure 4. Kosovo coal drying section.

The Kosovo plant is smaller than proposed first generation U.S. Lurgi gasification plants, but it contains many of the process units which are likely to be employed in those plants. For this reason, the plant is considered to be representative of the Lurgi facilities likely to be built in the U.S. in the near future.

While many of the process units employed at Kosovo are representative of those proposed for use in future U.S. Lurgi facilities, the environmental control practices followed at the Kosovo plant are not. Thus, while the discharges that enter the environment at Kosovo are not representative of those that would be encountered in similar U.S. facilities, the types of control problems facing U.S. Lurgi plant operators will be similar to those found at Kosovo. A study of the waste and process streams at the Kosovo plant should aid U.S. plant designers in developing the process modifications and control schemes necessary to achieve U.S. standards of environmental protection.

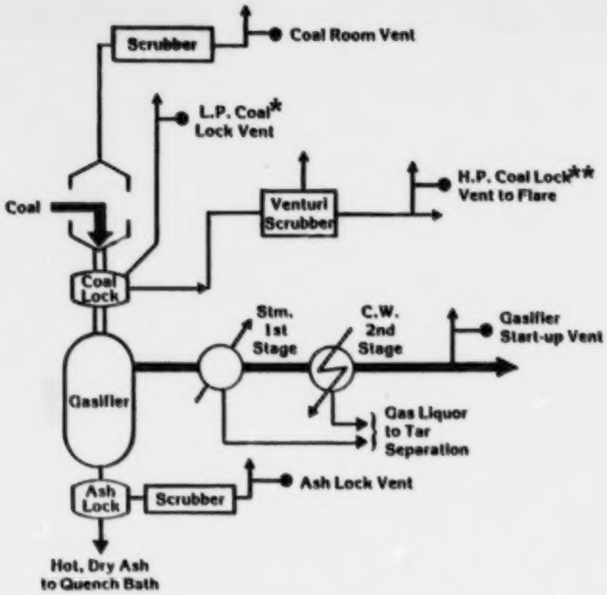
Test Rationale

The Kosovo gasification plant contains approximately 70 streams which have a significant potential for adversely impacting the environment. However, since the cost of characterizing such a large number of streams was considered prohibitive, during Phase I, approximately 50 streams were surveyed. In this survey, the major pollutants present in the process and uncontrolled discharge streams were identified. Based on these results, a limited number (20 to 30) of streams were selected for detailed study in Phase II.

Process and discharge streams were selected for study for one or more of the following reasons:

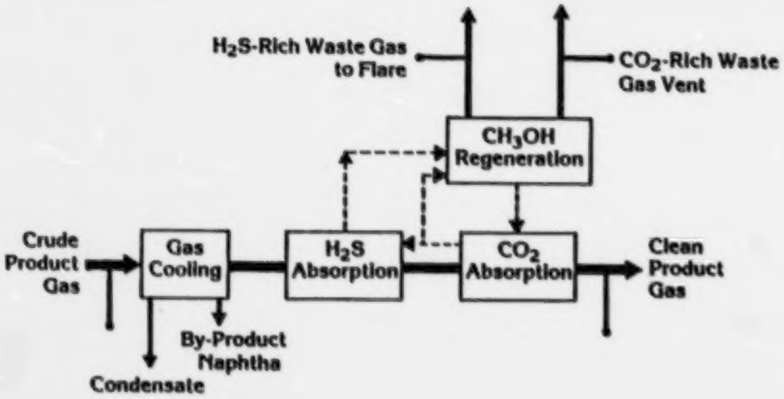
- high discharge rate,
- significant pollutant concentration,
- needed for trace pollutant fate determination, and/or
- provided useful process information.

Figures 4 through 10 show simplified flow schemes of the primary process units of the Kosovo plant. Streams selected for Phase II testing are identified in these figures.


Scrubber
Coal Room Vent
L.P. Coal*
Lock Vent
Venturi
Scrubber
H.P. Coal Lock**
Vent to Flare
Coal
Coal
Lock
Stm.
1st
Stage
C.W.
2nd
Stage
Gasifier
Start-up Vent
Gasifier
Gas Liquor
to Tar
Separation
Ash
Lock
Scrubber
Ash Lock Vent
Hot, Dry Ash
to Quench Bath

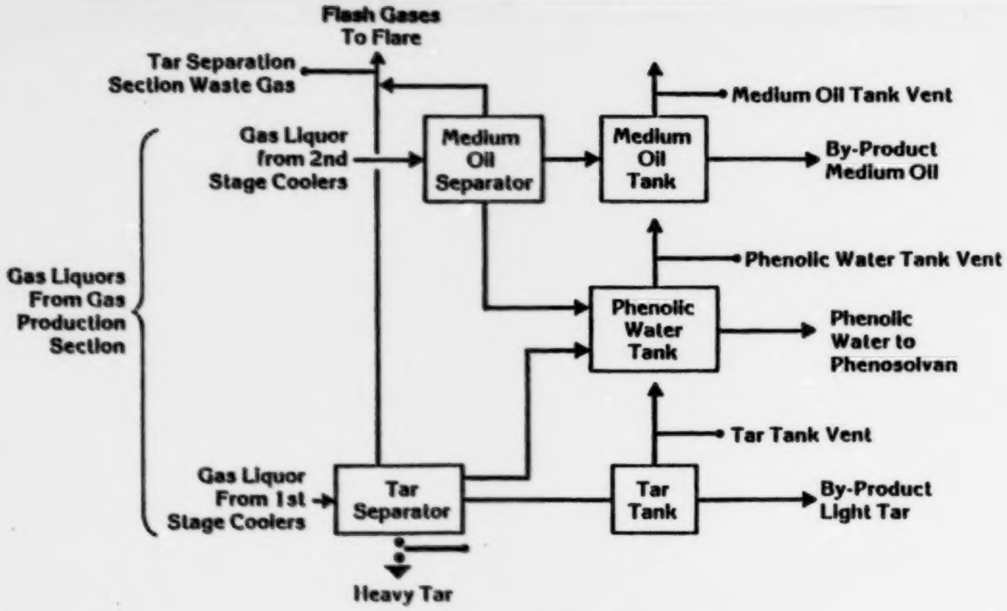
*L.P. - Low Pressure
**H.P. - High Pressure
——● - indicates sampling point

Figure 5. Kosovo Gas Production section.


H_2S-Rich Waste Gas
to Flare
CO_2-Rich Waste
Gas Vent
CH_3OH
Regeneration
Crude
Product
Gas
Gas
Cooling
H_2S
Absorption
CO_2
Absorption
Clean
Product
Gas
By-Product
Naphtha
Condensate

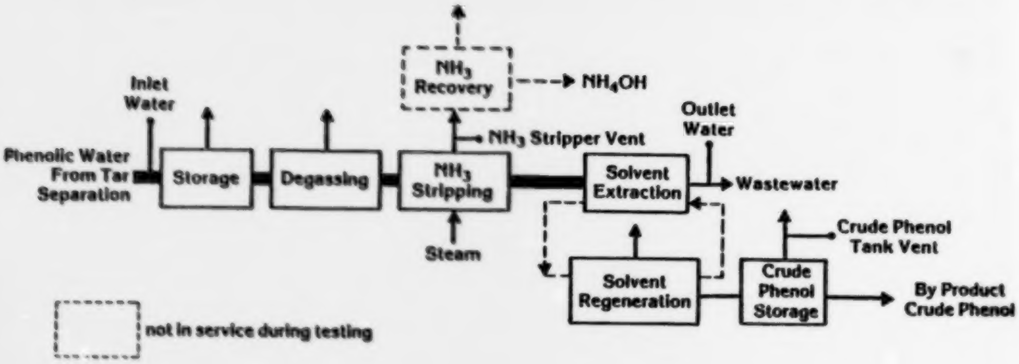
——● - indicates sampling point

Figure 6. Kosovo Rectisol section.


Flash Gases
To Flare
Tar Separation
Section Waste Gas
Medium Oil Tank Vent
Gas Liquor
from 2nd
Stage Coolers
Medium
Oil
Separator
Medium
Oil
Tank
By-Product
Medium Oil
Phenolic Water Tank Vent
Gas Liquors
From Gas
Production
Section
Phenolic
Water
Tank
Phenolic
Water to
Phenosolvan
Tar Tank Vent
Gas Liquor
From 1st
Stage Coolers
Tar
Separator
Tar
Tank
By-Product
Light Tar
Heavy Tar

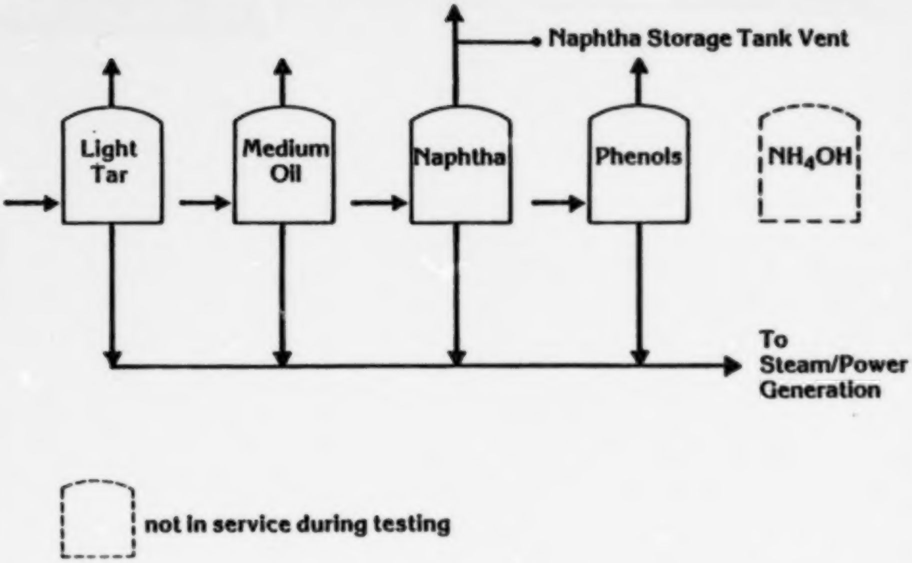
—• - indicates sampling point

Figure 7. Kosovo Tar Separation section.


NH_3
Recovery
NH_4OH
Inlet
Water
Outlet
Water
NH_3 Stripper Vent
Phenolic Water
From Tar
Separation
Storage
Degassing
NH_3
Stripping
Solvent
Extraction
Wastewater
Steam
Crude Phenol
Tank Vent
Solvent
Regeneration
Crude
Phenol
Storage
By Product
Crude Phenol
not in service during testing

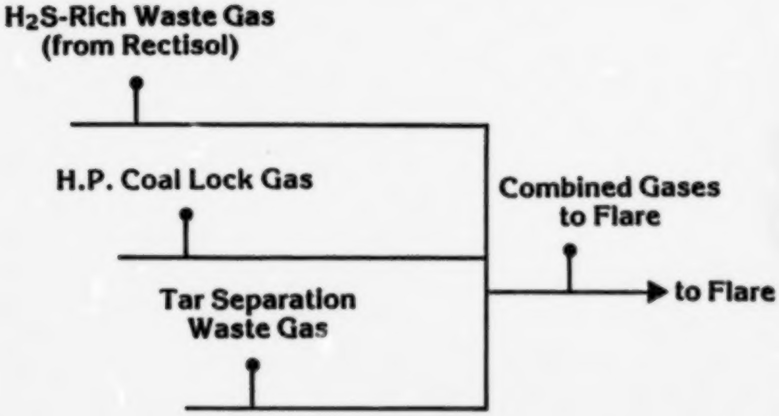
—• - indicates sampling point

Figure 8. Kosovo Phenosolvan section.


Naphtha Storage Tank Vent
Light Tar
Medium Oil
Naphtha
Phenols
NH_4OH
To Steam/Power Generation
not in service during testing

—• - indicates sampling point

Figure 9. Kosovo By-Product Storage section.


H_2S-Rich Waste Gas (from Rectisol)
H.P. Coal Lock Gas
Tar Separation Waste Gas
Combined Gases to Flare
to Flare

—• - indicates sampling point

Figure 10. Kosovo Flare Feed system.

Stream Parameters: The Phase I and Phase II characterization efforts addressed the following parameters:

Gaseous Streams

- Flow rate
- Particulate concentration
- Gas composition
- Condensible organics
- Trace elements

Aqueous Streams

- Water quality parameters
- Trace elements
- Organic constituents

Solids

- Proximate analyses
- Ultimate analyses
- Trace elements
- Leachate analyses

Liquid By-Products

- Bulk composition
- Trace elements

Sampling and Analytical Methods: With the exception of the condensible organics analysis, all gas stream characterization work was performed on-site. The methods used for gaseous sampling and analysis are listed in Table 1. Liquid and solid analyses were performed where applicable, with either EPA or ASTM standard methods. These methods are identified and discussed elsewhere (Ref. 3). New methods, developed specifically to characterize sulfur- and nitrogen-containing organic compounds in liquid by-products will be reported separately.

Data Evaluation - Source Analysis Model 1/A

The Source Analysis Model 1/A (SAM/1A) is a procedure developed by EPA-IERL for evaluating discharge stream data. Its principle strength is that it makes possible the reduction of pollutant discharge data to a common numerical base so that discharges can be ranked or prioritized.

TABLE 1. SAMPLING AND ANALYTICAL METHODS

Parameter	Collection Method	Analytical Method
CONDENSIBLE HYDROCARBONS:		
Condensible Hydrocarbons	Gas stream cooled to 0°C and resulting condensate trapped in impingers. The remaining condensible hydrocarbons trapped on XAD-2 resin.	Organic material extracted from condensate and resin with CH_2Cl_2. Extract analyzed with gas chromatography/mass spectrometry.
Benzene, Toluene, and Xylene	Vapors trapped from gas stream by activated carbon.	Vapors solvent extracted from carbon and analyzed by GC with flame ionization detector.
GASEOUS SPECIES BY GC:		
Fixed Gases (CO, H_2, CO_2, N_2, O_2, CH_4)	Sample was heated, filtered and dried then compressed into silanized glass bombs for analyses.	Gas chromatograph with thermal conductivity detector.
Hydrocarbons C_1 - C_6, C_6^+ Benzene, Toluene, and Xylene	Sample was heated, filtered and dried then compressed into silanized glass bombs for analyses.	Gas chromatograph with flame ionization detector.
Sulfur Species (H_2S, COS, CS_2, SO_2, Mercaptans)	Sample was heated, filtered and dried then compressed into silanized glass bombs for analyses.	Gas chromatograph with flame photometric detector.

(Continued)

TABLE 1 (Continued). SAMPLING AND ANALYTICAL METHODS

Parameter	Collection Method	Analytical Method
PARTICULATE:		
Suspended Particulate	EPA Method 5, gas filtered at 250°F out of stack.	Gravimetric.
	EPA Method 17, gas filtered at duct temperature in stack.	Gravimetric.
Suspended Particulate Plus Condensibles	Condensation and collection in a series of water filled impingers.	Filtration, extraction with CH_2Cl_2, Gravimetric.
TRACE ELEMENTS:		
Non-Volatile Elements (Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sr, Tl, V, Zn)	Two impingers with 10% HNO_3 followed by two impingers with 10% NaOH.	Dissolution, AA with Graphite Furnace.
Volatile Elements (Hg, As, Sb, Se)	Two impingers with 10% HNO_3 followed by two impingers with 10% NaOH.	Dissolution, AA with Hydride Generation.
Iron and Nickel Carbonyls	Two fritted impingers with 3% HCl.	AA with Graphite Furnace.
OTHER GASES:		
Ammonia	Two fritted impingers with 0.1 N H_2SO_4.	Distillation into boric acid and back titration with sulfuric acid.

(Continued)

TABLE 1[*](Continued). SAMPLING AND ANALYTICAL METHODS

Parameter	Collection Method	Analytical Method
Hydrogen Sulfide	Two fritted impingers with 0.1 N cadmium acetate.	Iodine addition and back titration with thiosulfate.
Hydrogen Cyanide	Two fritted impingers with 0.1 N cadmium acetate followed by two fritted impingers with 0.1 N NaOH.	Distillation and titration with silver nitrate.
Phenols	Two fritted impingers with 0.1 N NaOH.	Spectrophotometric determination by reaction with 4-aminoantipyrine.

The SAM/1A model is based upon the use of discharge multimedia environmental goals (DMEG's) to compute Discharge Severity (DS) values (Ref. 4). DMEG's are concentration levels below which the discharged component is of low concern for its potential effects on either human health or the ecology. Thus, it is a "target value" for components in discharge streams. DMEG's have been defined for many substances representing 26 classes of organic compounds (Ref. 5). Target levels have been defined in terms of their effect on both human health and ecology for discharges to the three environmental media: air, water, and soil. DMEG (Air/Health) values for 16 components whose concentrations were measured in this study, are shown graphically in Figure 11. A reciprocal of DMEG is plotted since DS is the product of concentration and 1/DMEG as defined below:

$$\text{DS} = \frac{\text{Measured Concentration of a Pollutant}}{\text{DMEG of that Pollutant}}$$

Since the DMEG allows the severity of different compounds to be related to a common numerical base ("multiples of the target value"), a stream's total discharge severity (TDS) can be determined by summing the DS values for all components in that stream:

$$\text{TDS} = \sum \text{DS}.$$

The TDS value provides a basis for comparing uncontrolled discharge streams, and, therefore, provides a basis for identifying the most severe (highest TDS) streams.

Discharge severity is a concentration - based value that does not take into account the quantity of mass emitted. Used alone it cannot define the environmental effects of a discharge because such effects are related to both quantity and severity. With the SAM/1A Model, the environmental significance of a pollutant in a given discharge stream is defined by its Weighted Discharge Severity (WDS):

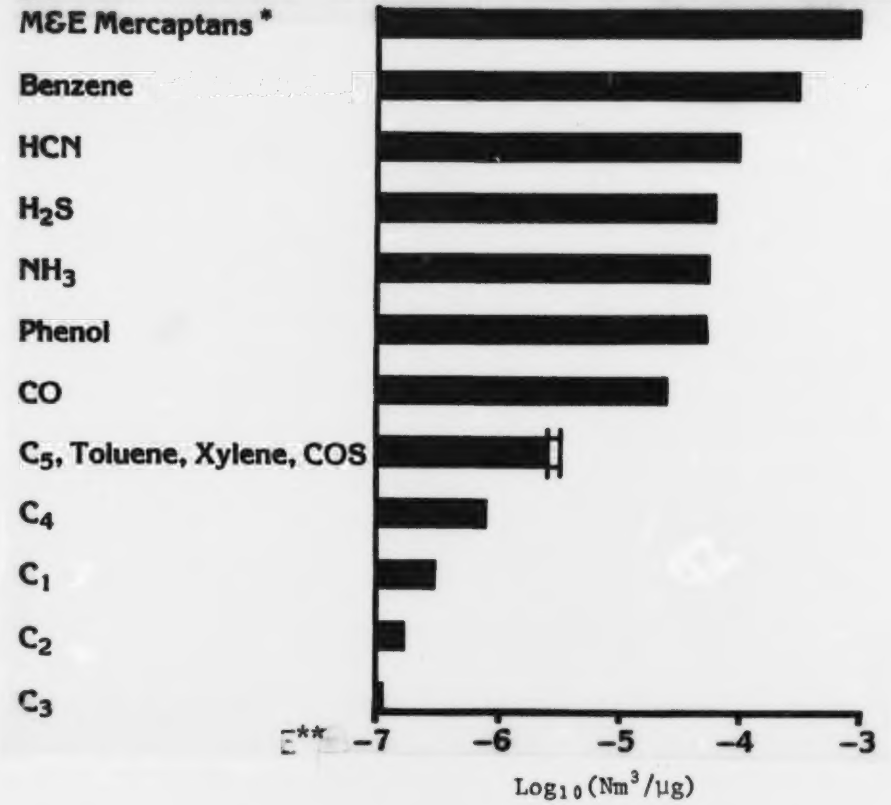
$$\text{WDS} = \text{F} \cdot \text{DS}$$

where F = Stream Flow Rate;

and further, the environmental significance of that discharge stream is defined by its Total Weighted Discharge Severity (TWDS):

$$\text{TWDS} = \text{F} \cdot \sum \text{DS} = \text{F} \cdot \text{TDS}$$

By comparing discharge streams within a given medium, such as gaseous, aqueous, or solid, the stream with the highest TWDS value may be selected as the most environmentally significant.



*Methyl and Ethyl Mercaptans

E** = Exponential (E-5 = 10^{-5})

Figure 11. Key Kosovo gaseous pollutants in order of severity (1/DMEG).

Results and Discussion

The results obtained during the Kosovo study consist of stream composition and flow rate data. The data presented and discussed in this section were selected from Phases I and II as "best values" based on engineering and analytical judgment. The results discussed here are for the streams selected for detailed examination in the Phase II test program.

Gaseous Streams: Test data for gaseous streams are presented in Tables 2 and 3. In Table 2, the concentration data are given in molar concentration units (vol % or ppmv) while in Table 3, these data are expressed in mass concentration units ($\mu g/m^3$). Oxygen and nitrogen analyses were included in the fixed gas analyses for quality control. Samples showing abnormal levels of O_2 and N_2 (indicating an air leakage into the sample) were resampled.

The data in Table 3 were used to calculate the mass discharge rate from each stream for each major pollutant. Table 4 summarizes the streams having the highest concentration and those having the highest mass flow for each type of pollutant measured. As this table shows, a single stream, such as the ammonia stripper vent, can be the source of several pollutants at comparatively high concentrations. The table also indicates that the H_2S-rich waste gas and CO_2-rich waste gas streams are of concern because of the high flow rates of these streams. In addition, the by-product tank vents (naphtha storage tank, medium oil tank, phenolic water tank) are significant because of high pollutant concentrations.

Figure 12 shows a graphic representation of the mass flow rate of the major gaseous pollutants. As shown, C_1 to C_6+ hydrocarbons and sulfur species pollutants are produced in the largest quantities. Most of the sulfur species are sent to the flare, whereas most of the ammonia and phenols are discharged directly to the atmosphere. The C_1 to C_6+ hydrocarbons are well distributed among most of the flare feed and uncontrolled discharge streams.

Discharge severity values accent pollutants of greatest concern in terms of their potential to cause adverse health or environmental effects. Figure 13 illustrates the relationship between DS values and pollutant mass concentration data for the major pollutants in the coal lock vent discharge. Note that BTX (benzene, toluene, and xylene) and mercaptans, which are at relatively low concentrations (Figure 13A), emerge as pollutants of high concern when the severity of the discharge is investigated (Figure 13B).

TABLE 2. KOSOVO GASEOUS STREAM COMPOSITION DATA

PLANT SECTION:	**GAS PRODUCTION**			**RECTISOL**			
SAMPLE POINT:	3.2 Low Pressure Coal Lock Vent	3.3 Gasifier Start-up Vent	3.6 High Pressure Coal Lock (Flare Feed Stream)	7.1 H_2S-rich Waste Gas (Flare Feed Stream)	7.2 CO_2-rich Waste Gas Vent	7.3 Crude Gas (Process Stream)	7.4 Product Gas (Process Stream)
Dry Gas Flow Rate (m^3/gasifier-hr @ 25°C)	21	-	230	3600	3600	18,800*	13,100*
Temperature (°C)	56	-	54	12	19	22	-
Moisture Content (%)	44	70	11	3.9	5.1	2.5	4.1
Molecular Wt. of Dry Gas	23.5	33.1	24.9	43.0	42.2	21.9	10.3
Composition (Dry Basis)							
Fixed Gases (Vol %)							
N_2	37	0.09	32	0.11	Tr	38.1	60
O_2	0.27	4.5	0.24	Tr	Tr	0.36	0.44
H_2	0.18	42	0.14	Tr	Tr	0.64	0.38
CH_4	8.6	1.6	10.5	4.3	1.2	11.5	16
CO	14.6	14	12	1.1	Tr	15	22
CO_2	36.5	34	42	88	94	32	0.02
Sulfur Species (ppmv)							
H_2S	13,000	6300	3500	45,400	39	6000	NF
COS	110	110	120	420	62	97	0.17
CH_3SH	420	490	460	2100	8.5	590	1.1
C_2H_5SH	220	240	210	780	4.4	200	1.0
Hydrocarbons (Vol %)							
C_2H_4	0.22	0.15	0.42	0.82	1.6	0.47	0.15
C_2H_6	Tr	0.05	Tr	Tr	Tr	0.04	Tr
C_3's	0.14	0.08	0.25	0.63	0.28	0.19	Tr
C_4's	0.05	0.03	0.11	0.32	Tr	0.074	Tr
C_5's	Tr	0.007	0.01	0.04	Tr	0.044	Tr
C_6+	0.12	0.09	0.08	0.21	NF	0.064	0.03
Aromatic Species (ppmv)							
Benzene	760	90	550	110	1.0	750	-
Toluene	220	10	100	8	Tr	230	-
Xylene & Ethylbenzene	75	Tr	38	NF	Tr	100	-
Phenols	5.7	630	2.5	Tr	NF	Tr	Tr
Higher Aromatics	-	-	-	-	-	-	-
Nitrogen Species (ppmv)							
NH_3	2400	11,000	NF	3200	4.6	3.3	Tr
HCN	600	2,900	170	200	13	320	-

Tr - Trace = 0.01 vol. % for fixed gases, 1 ppmv for all others.
NF - Not Found = less than a trace.
* = Design Value.
- = No Data Available.

(Continued)

TABLE 2 (Continued). KOSOVO GASEOUS STREAM COMPOSITION DATA

PLANT SECTION:	TAR SEPARATION				PHENOSOLVAN	BY-PRODUCT STORAGE	FLARE SYSTEM
SAMPLE POINT:	13.1 Tar Tank Vent	13.3 Medium Oil Tank Vent	13.6 Tar Separation Waste Gas(Flare Feed Stream)	13.7 Phenolic Water Tank Vent	14.5 NH_3 Stripper Vent	15.3 Naphtha Storage Tank Vent	20.1 Combined Gas to Flare
Dry Gas Flow Rate (m^3/gasifier-hr @ 25°C)	0.55	1.7	28*	5.5	260	4.5	1330
Temperature (°C)	52	42	40	76	91	32	21
Moisture Content (%)	14	8.4	7.7	42	76	5	2.5
Molecular Wt. of Dry Gas	29.1	32.5	39.0	34.4	32.7	33.3	41.7
Composition (Dry Basis)							
Fixed Gases (Vol %)							
H_2	Tr	Tr	11	Tr	NF	NF	Tr
O_2	19	0.45	Tr	13	-	2.6	0.10
N_2	77.5	1.1	Tr	39	-	84	0.21
CH_4	0.16	7.6	3.5	0.2	Tr	NF	6.2
CO	Tr	5.9	1.1	NF	NF	NF	1.9
CO_2	0.86	56	77.5	35	55	0.85	88
Sulfur Species (ppmv)							
H_2S	6900	26,000	9000	12,600	19,500	NF	10,600
COS	110	96	120	41	NF	NF	250
CH_3SH	390	5200	2500	2100	290	2600	2500
C_2H_5SH	240	2100	1600	7200	100	9700	190
Hydrocarbons (Vol %)							
C_2H_6	Tr	0.34	0.33	} 0.02	} Tr	} Tr	0.77
C_2H_4	-	Tr	Tr				Tr
C_3's	0.01	0.30	0.41	0.02	Tr	0.01	0.65
C_4's	Tr	0.25	0.41	0.02	Tr	0.07	0.38
C_5's	Tr	0.09	0.09	0.006	Tr	0.08	0.04
C_6+	0.37	2.4	1.3	1.8	NF	5.3	0.06
Aromatic Species (ppmv)							
Benzene	2000	7650	9600	11,000	Tr	37,600	640
Toluene	960	1400	1200	2300	-	1900	215
Xylene & Ethylbenzene	220	140	150	280	Tr	60	33
Phenols	57	110	4.2	Tr	6200	Tr	Tr
Higher Aromatics	2.2	-	4.9	3.1	-	-	-
Nitrogen Species (ppmv)							
NH_3	2600	19	19,300	12,000	418,000	NF	NF
HCN	130	57	64	38	4800	1100	100

Tr - Trace = 0.01 vol. % for fixed gases, 1 ppmv for all others.
NF - Not Found = less than a trace.
* = Design Value.
- = No Data Available.

TABLE 3. COMPONENT CONCENTRATIONS IN KOSOVO GASEOUS STREAMS

PLANT SECTION:	GAS PRODUCTION		RECTISOL			
SAMPLE POINT:	3.2 Low Pressure Coal Lock Vent	3.6 High Pressure Coal Lock Vent (Flare Feed Stream)	7.1 H_2S-Rich Waste Gas (Flare Feed Stream)	7.2 CO_2-Rich Waste Gas Vent	7.3 Crude Product Gas	7.4 Clean Product Gas
Component (μg/m³ @ 25°C)						
Fixed Gases						
H_2	3.05E07	2.64E07	9.06E04	Tr	3.14E07	4.94E07
O_2	3.53E06	3.14E06	Tr	Tr	4.70E06	5.75E06
N_2	2.06E06	1.60E06	Tr	Tr	7.32E06	4.35E06
CH_4	5.64E07	6.88E07	2.82E07	7.84E06	7.54E07	1.05E08
CO	1.67E08	1.37E08	1.26E07	Tr	1.71E08	2.52E08
CO_2	6.56E08	7.55E08	1.58E09	1.69E09	5.81E08	3.60E05
Sulfur Species						
H_2S	1.81E07	4.87E06	6.32E07	5.43E04	8.35E06	NF
COS	2.70E05	2.95E05	1.03E06	1.52E05	2.38E05	4.17E02
CH_3SH	8.25E05	9.04E05	4.13E06	1.67E04	1.16E06	2.16E03
C_2H_5SH	5.57E05	5.33E05	1.98E06	1.12E04	5.08E05	2.54E03
Hydrocarbons						
C_2H_6	2.70E06	5.16E06	1.01E07	1.97E07	5.77E06	1.84E06
C_2H_4	Tr	Tr	Tr	Tr	4.58E05	Tr
C_3's	2.52E06	4.50E06	1.14E07	5.04E06	3.42E06	Tr
C_4's	1.19E06	2.61E06	7.60E06	Tr	1.76E06	Tr
C_5's	Tr	2.95E05	1.18E06	Tr	1.30E06	Tr
C_6+	4.22E06	2.82E06	7.39E06	NF	2.25E06	1.06E06
Benzene	2.43E06	1.76E06	3.51E05	3.19E03	2.39E06	-
Toluene	8.38E05	3.76E05	3.00E04	Tr	8.66E05	-
Xylene & Ethylbenzene	3.25E05	1.65E05	NF	Tr	4.34E05	-
Phenols	2.19E04	9.61E03	Tr	NF	Tr	Tr
Nitrogen Species						
NH_3	1.67E06	NF	1.53E06	3.20E03	2.30E03	Tr
HCN	6.62E05	1.88E05	2.21E05	1.44E04	3.53E05	-
Dry Gas Flow Rate (m³/gasifier-hr @ 25°C)	21	230	3,600	3,600	18,800*	13,100*

NF = Not Found
Tr = Trace
* = Design Value

(Continued)

TABLE 3 (Continued). COMPONENT CONCENTRATIONS IN KOSOVO GASEOUS STREAMS

PLANT SECTION:	TAR SEPARATION				PHENOSOLVAN	BY-PRODUCT STORAGE	FLARE SYSTEM
SAMPLE POINT:	13.1 Tar Tank Vent	13.2 Medium Oil Tank Vent	13.6 Tar Separation Waste Gas (Flare Feed Stream)	13.7 Phenolic Water Tank Vent	14.5 Ammonia Stripper Vent	15.3 Naphtha Storage Tank Vent	20.1 Combined Gas to Flare
Component (μg/m³ @ 25°C)							
Fixed Gases							
H_2	Tr	Tr	9.06E06	Tr	NF	NF	Tr
O_2	2.48E08	5.88E06	Tr	1.70E08	-	3.40E07	1.31E06
N_2	8.87E08	1.26E07	Tr	4.46E08	-	9.61E08	2.40E06
CH_4	1.04E06	4.98E07	2.29E07	1.31E06	Tr	NF	4.06E07
CO	Tr	6.75E07	1.26E07	NF	NF	NF	2.17E07
CO_2	1.55E07	1.01E09	1.40E09	6.29E08	9.89E08	1.53E07	1.58E09
Sulfur Species							
H_2S	9.61E06	3.62E07	1.25E07	1.75E07	2.72E07	NF	1.48E07
COS	2.70E05	2.36E05	2.94E05	1.01E05	NF	NF	6.14E05
CH_3SH	7.66E05	1.02E07	4.91E06	4.13E06	5.70E05	5.11E06	4.91E06
C_2H_5SH	6.09E05	5.33E06	4.06E06	1.83E07	2.54E05	2.46E07	4.82E05
Hydrocarbons							
C_2H_6	Tr	4.18E06	4.05E06	2.46E05	Tr	Tr	9.46E06
C_2H_4	-	Tr	Tr	-	-	-	Tr
C_3's	1.80E05	5.40E06	7.39E06	3.60E05	Tr	1.80E05	1.17E07
C_4's	Tr	5.94E06	9.74E06	4.75E05	Tr	1.66E06	9.03E06
C_5's	Tr	2.65E06	2.65E06	1.77E05	Tr	2.36E06	1.18E06
C_6+	1.30E07	8.45E07	4.58E07	6.34E07	NF	1.87E08	2.11E06
Benzene	6.38E06	2.44E07	3.06E07	3.51E07	-	1.20E08	2.04E06
Toluene	3.61E06	5.27E06	4.52E06	8.66E06	-	7.15E06	8.09E05
Xylene & Ethylbenzene	9.54E04	6.06E05	6.51E05	1.21E06	Tr	2.60E05	1.43E05
Phenols	2.19E05	4.24E05	1.62E04	Tr	2.38E07	Tr	Tr
Nitrogen Species							
NH_3	1.81E06	1.32E04	1.34E07	8.35E06	2.91E08	NF	NF
HCN	1.44E05	6.28E04	7.05E04	4.20E04	5.30E06	1.21E06	1.10E05
Dry Gas Flow Rate (m³/gasifier-hr @ 25°C)	0.55	1.7	28*	5.5	260	4.5	1,330

NF = Not Found
Tr = Trace
* = Design Value

TABLE 4. MAJOR KOSOVO DISCHARGE STREAMS BASED ON POLLUTANT CONCENTRATION AND MASS FLOW RATE

Pollutant	HIGHEST CONCENTRATION		GREATEST MASS FLOW RATE	
	Direct Atmospheric Discharges	Total Plant*	Direct Atmospheric Discharges	Total Plant*
CO	LP Coal Lock Vent	LP Coal Lock Vent	LP Coal Lock Vent	H_2S-Rich Waste Gas
$C_1 - C_6$	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	CO_2-Rich Waste Gas Vent	H_2S-Rich Waste Gas
BTX†	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	Phenolic Water Tank Vent	Tar Separation Waste Gas
Total Sulfur Species	Medium Oil Tank Vent Naphtha Storage Tank Vent Phenolic Water Tank Vent	H_2S-Rich Waste Gas	Ammonia Stripper Vent	H_2S-Rich Waste Gas
H_2S	Medium Oil Tank Vent	H_2-S-Rich Waste Gas	Ammonia Stripper Vent	H_2S-Rich Waste Gas
COS	LP Coal Lock Vent	H_2S-Rich Waste Gas	CO_2-Rich Waste Gas	H_2S-Rich Waste Gas
Mercaptans	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	Ammonia Stripper Vent	H_2S-Rich Waste Gas
Phenols	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent
NH_3	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent
HCN	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent

*Includes both direct discharge and flare feed streams.
†Benzene, Toluene, and Xylenes.

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Figure 12A.

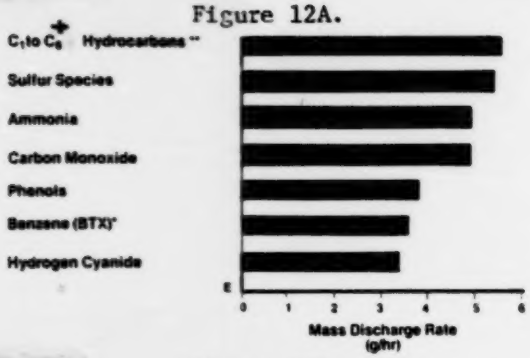


Figure 12B.

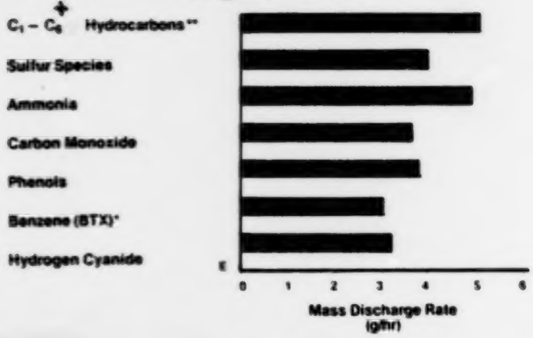
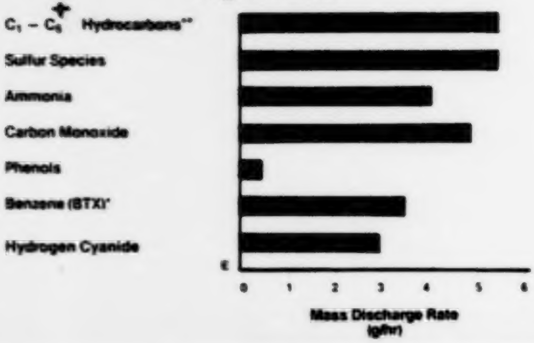
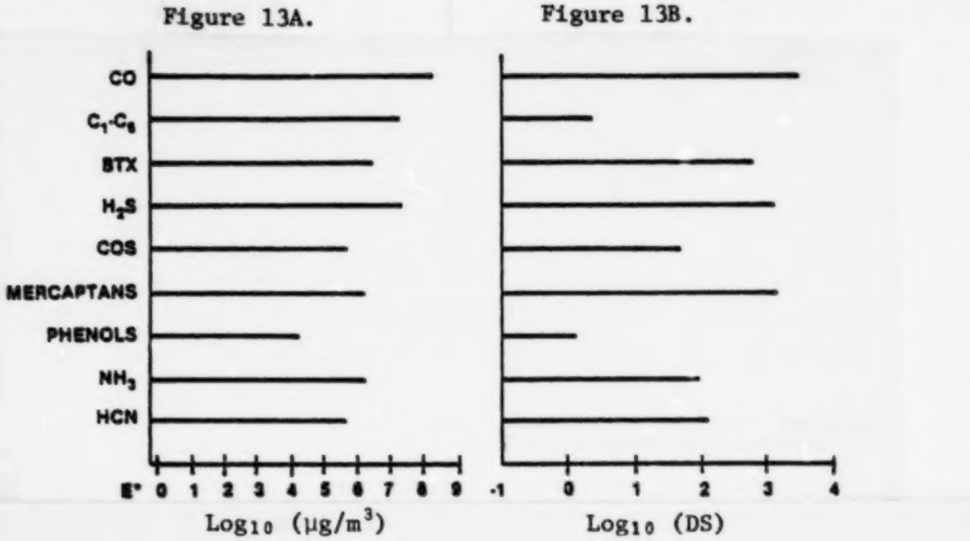


Figure 12C.



*BTX = Benzene, Toluene, Xylenes
**Excluding Benzene
A. Plant-Wide Discharge and Flare Feed Streams
B. Discharge Streams Only
C. Flare Feed Streams Only

Figure 12. Total mass flow rate in Kosovo Gaseous Streams.



Mass concentration of pollutants in LP coal lock vent

Discharge Severity of pollutants in LP coal lock vent

*Exponential (E05 = 10^5)

Figure 13. Comparison of mass concentrations with calculated discharge severities in the low pressure coal lock vent discharge stream.

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X

Discharge severity values for the individual pollutants and total stream discharge severity values for the plant's key gaseous streams are listed in Table 5. Figure 14 shows a comparison of these total stream discharge severities for the seven uncontrolled discharge streams examined during Phase II. From this comparison it is evident that the discharge from the naphtha storage tank vent is several hundred times more severe (DS on the order of 70,000) than the discharge from the CO_2-rich waste gas vent (DS on the order of 200). However, when the flow rates of the respective streams are taken into consideration, the two streams have comparable TWDS values as is illustrated in Figure 15. The relationship of flow rate and TDS to TWDS is illustrated well in Figure 15 for the seven uncontrolled streams. Since the bar graphs are plotted on a log scale, the sum of the logs of the flow component and the TDS component equals the log of the TWDS. From this plot, streams can be prioritized according to flow rate, DS, or TWDS:

- Largest Stream (highest flow rate) - CO_2-rich waste gas vent.
- Most Severe Stream (highest TDS) - Naphtha storage tank vent.
- Most Environmentally Significant Stream (highest TWDS) - Ammonia stripper vent.

Figure 15 illustrates why the very large stream with a low TDS value (CO_2-rich waste gas) and the very small stream with a high TDS value (tar tank) are both environmentally significant (TWDS values are comparable).

Pollutant WDS values from the seven uncontrolled discharge streams are shown in Figure 16. This prioritization indicates that, of the pollutants discharged from the Kosovo plant, ammonia and sulfur species (H_2S and mercaptans) are the most environmentally significant (highest WDS values).

Particulates in Gaseous Streams: Particulate loadings were measured in six gaseous discharge streams. Except for the coal room vent (a dry stream), all measurements were made by the wet impinger method. In this method, particulates are collected as three fractions:

- filterable solids,
- dissolved solids, and
- tars and oils (condensible organics).

TABLE 5. DISCHARGE SEVERITY DATA FOR KOSOVO GASEOUS DISCHARGE STREAMS

PLANT SECTION:	GAS PRODUCTION			RECTISOL		TAR SEPARATION	
SAMPLE POINT: Component Discharge Severities	3.2 Low Pressure Coal Lock Vent	3.3 Gasifier Start Up Vent	3.6 High Pressure Coal Lock (Flare Feed Stream)	7.1 H_2S-Rich Waste Gas (Flare Feed Stream)	7.2 CO_2-Rich Waste Gas Vent	13.1 Tar Tank Vent	13.3 Medium Oil Tank Vent
Fixed Gases							
CH_4	1.70E01	3.20E-00	2.10E01	8.53E00	2.44E00	1.72E-01	1.50E01
CO	4.20E03	4.00E03	3.43E03	3.14E02	2.90E00	2.90E00	1.70E03
CO_2	7.30E01	6.80E01	8.40E01	1.76E02	1.88E02	1.71E00	1.12E02
Sulfur Species							
H_2S	1.20E03	5.84E02	3.24E02	4.21E03	3.61E00	6.40E02	2.41E03
COS	6.13E-01	6.13E-01	6.70E-01	2.34E00	3.34E-01	6.13E-01	5.40E-01
CH_3SH	8.30E02	9.62E02	9.03E02	4.12E03	1.70E01	7.70E02	1.02E04
C_2H_5SH	5.60E02	6.10E02	5.33E02	2.00E03	1.11E01	6.10E02	5.33E03
Hydrocarbons							
C_2H_4	4.42E-01	3.02E-01	8.50E-01	1.70E00	3.22E00	2.01E-04	6.84E-01
C_2H_6	2.01E-04	-	2.01E-04	2.01E-04	2.01E-04	-	2.01E-04
C_3's	2.80E-01	1.60E-01	5.00E-01	1.30E00	5.60E-01	2.00E-02	6.00E-01
C_4's	8.50E-01	5.10E-01	1.90E-00	5.42E00	1.70E-03	1.70E-03	4.24E00
C_5's	8.41E-03	5.90E-01	8.41E-01	3.40E00	8.41E-03	8.41E-03	7.60E00
C_6+	1.20E01	9.10E00	8.04E00	2.11E01	-	3.72E01	2.41E02
Aromatic Species							
Benzene	8.10E02	9.60E01	5.90E02	1.20E02	1.10E00	2.12E03	8.13E03
Toluene	2.20E00	7.60E-01	9.90E-01	7.90E-02	9.94E-03	9.51E00	1.40E01
Xylene and Ethylbenzene (as xylene)	7.40E-01	-	3.74E-01	-	1.40E-02	2.20E-01	1.40E00
Phenols (as Phenol)	1.20E00	1.30E02	5.10E-01	-	-	1.16E01	2.22E01
Nitrogen Species							
NH_3	9.30E01	4.30E02	-	8.50E01	1.77E-01	1.00E02	7.32E-01
HCN	6.02E01	2.91E02	1.70E01	2.00E01	1.30E00	1.30E01	5.71E00
Total Stream Discharge Severity	7.88E03	7.19E03	5.92E03	1.11E04	2.32E02	4.31E03	2.82E04
Dry Gas Flow Rate (m^3/gasifier-hr@25°C)	21.0	-	230	3600	3600	0.55	1.7
Total Weighted Discharge Severity (m^3/gasifier-hr@25°C)	1.65E05	-	1.36E06	3.99E07	8.37E05	2.20E03	4.79E04

(Continued)

TABLE 5 (Continued). DISCHARGE SEVERITY DATA FOR GASEOUS DISCHARGE STREAMS AT KOSOVO

PLANT SECTION:	TAR SEPARATION		PHENOSOLVAN	BY-PRODUCT STORAGE	FLARE SYSTEM
SAMPLE POINT:	13.6	13.7	14.5	15.3	20.1
Component Discharge Severities	Tar Separation Waste Gas (Flare Feed Stream)	Phenolic Water Tank Vent	Ammonia Stripper Vent	Naphtha Storage Tank Vent	Combined Gas to Flare
Fixed Gases					
CH_4	7.00E00	4.00E-01	2.00E-02	-	1.23E01
CO	3.14E 02	-	-	-	5.43E02
CO_2	1.56E 02	7.00E01	1.10E02	1.70E00	1.76E02
Sulfur Species					
H_2S	8.40E02	1.20E03	2.00E03	NF	9.84E02
COS	6.70E-01	2.30E-01	-	-	1.40E00
CH_3SH	4.10E03	4.12E03	6.30E02	5.10E03	4.91E03
C_2H_5SH	4.91E03	1.82E04	2.80E02	2.50E04	4.82E02
Hydrocarbons					
C_2H_6	6.64E-01	4.02E-02	9.5E-03	2.01E-04	1.50E00
C_2H_4	2.01E-04	-	-	-	2.01E-04
C_3's	8.20E-01	4.00E-02	2.00E-04	2.00E-02	1.32E00
C_4's	7.00E00	3.40E-01	1.70E-03	1.20E00	5.42E00
C_5's	7.60E00	5.10E-01	8.41E-03	6.73E00	3.40E00
C_6+	1.30E02	1.81E02	1.00E-02	5.33E02	1.00E01
Aromatic Species					
Benzene	1.02E04	1.20E04	-	4.00E04	6.80E02
Toluene	1.20E01	2.30E01	-	1.90E01	2.12E00
Xylene & Ethylbenzene (as xylene)	1.50E00	2.80E00	2.30E-06	5.91E-01	3.30E-01
Phenols (as Phenol)	8.50E-01	2.04E-05	1.40E03	5.30E-05	5.30E-05
Nitrogen Species					
NH_3	7.44E02	4.63E02	1.61E04	-	-
HCN	6.40E00	3.81E00	5.31E02	1.10E02	1.00E01
Total Stream Discharge Severity	2.06E04	3.67E04	2.07E04	7.08E04	1.22E04
Dry Gas Flow Rate (m^3/gasifier-hr @ 25°C)	28	5.5	260	4.5	1330
Total Weighted Discharge Severity (m^3/gasifier-hr @ 25°C)	7.66E05	2.02E06	5.39E06	3.19E05	1.62E07

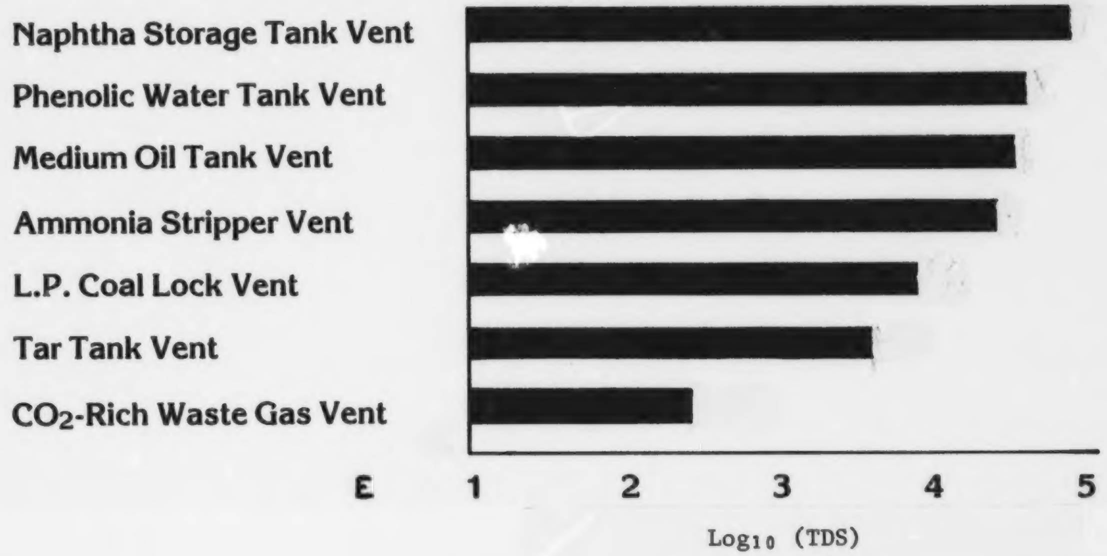


Figure 14. Key Kosovo gaseous discharge streams in order of decreasing TDS.

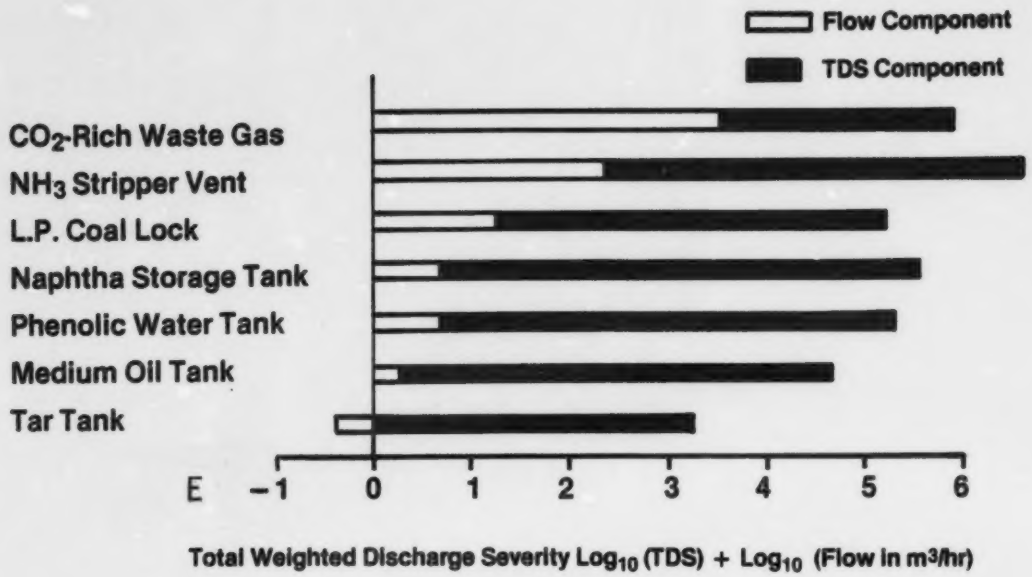
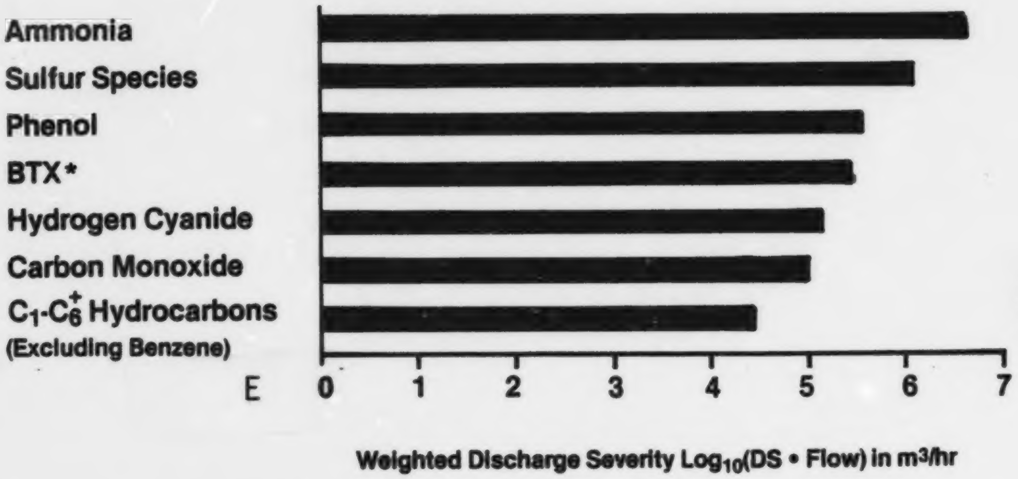


Figure 15. TWDS for key Kosovo gaseous discharge streams.



*Benzene, Toluene, and Xylenes

Figure 16. Most significant gaseous pollutants (plant-wide) in uncontrolled discharge streams.

The particulate data are shown in Table 6. This discussion will focus on the results from the impinger collections and particularly on those collected from the LP coal lock vent. This stream is emphasized because of the potential environmental significance of the particulates that it transports.

As indicated below, a major portion of the particulate catch from most gaseous streams consisted of condensed organics (tars and oils):

Stream	Tars and Oils (Wt % in Particulates)
LP coal lock vent	90
Gasifier start-up vent	95
HP coal lock vent	69
Tar separation waste gases	72
Combined gas to flare	76

Analytical results are not yet available from these collections; however, by-product analysis data can be used to make judgments about the significance of these particulates. For example, the LP coal lock vent discharge contained 8.1E06 $\mu g/m^3$ of particulates of which 7.3E06 $\mu g/m^3$ were tars and oils. In order to provide an estimate of the PNA content of the particulates in this stream, it was assumed that the PNA concentrations in the condensed organic fraction of the particulates (tars and oils) were the same as the PNA concentrations in the by-product tars and oils. Table 7 shows the concentrations of several of the most severe PNA's contained in the light tar and the medium oil. Using the following data:

LP Coal Lock Vent	Concentration $\mu g/m^3$	Mass Flow g/hr
Total Particulate	8.1E06	1.7E08
Tars and Oils in Particulate	7.3E06	1.5E08
Benzo(a)pyrene based on BaP in tar	1.5E03	3.2E04
Benzo(a)pyrene based on BaP in medium oil	0.5E03	1.0E04

the calculated concentration level of benzo(a)pyrene in the LP coal lock vent discharge is in the range of 500 to 1,500 $\mu g/m^3$. This level of PNA's will increase the TWDS of the LP coal lock vent significantly. The effects of PNA's upon the TWDS values of key streams (using the average PNA content of light tar and medium oil) are shown in Figure 17. Note that the increase in TDS (and TWDS) by the inclusion of the PNA data elevates the LP coal lock vent to the same order of magnitude as the ammonia stripper vent and identifies it as the second most environmentally significant of the uncontrolled discharge streams at Kosovo (excluding flare feed streams - H_2S-rich waste gas, and HP coal lock vent).

TABLE 6. PARTICULATE CONCENTRATION DATA FOR KOSOVO GASEOUS STREAMS

STREAM TYPE:	DISCHARGE STREAMS			FLARE FEED STREAMS		
SAMPLE POINT:	2.2 Coal Room Vent	3.2 Low Pressure Coal Lock Vent	3.3 Gasifier Start-Up Vent	3.6 High Pressure Coal Lock Vent	13.6 Tar Separation Waste Gas	20.1 Combined Gases to Flare
Dry Gas Flow Rate (m^3/gasifier-hr @ 25°C)	7200	21	*	230	28	1330
Total Particulate (mg/m^3 @ 25°C)	98	8100	9450	960	920	410
Condensed Organics (Tars and Oils)	**	7300	8980	660	660	310
Dissolved Solids	**	650	400	240	230	54
Filtered Solids	**	220	61	61	29	47

* - Variable Flow Rate.
** - Dry Stream; Analysis Not Applicable.

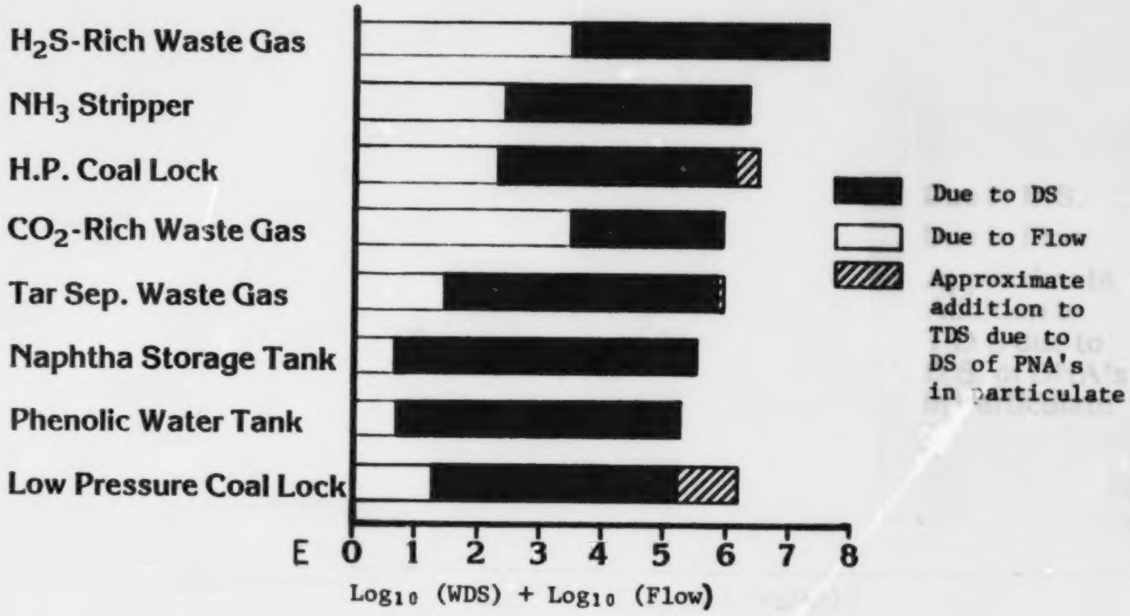


Figure 17. Total weighted discharge severity for key Kosovo gaseous streams.

TABLE 7. PNA'S IN KOSOVO LIGHT TAR AND MEDIUM OIL (μg/g)

Compound	Light Tar	Medium Oil
7,12-Dimethylbenz(a)anthracene	1,100	62
Benz(a)anthracene	490	160
Benzo(b)fluorene	310	120
Benzo(a)pyrene	210	68
Dibenzo(a)anthracene	23	7
3-methylcholanthrene	26	NF
252 Group	950*	280*

*Benzo(a)pyrene concentration = 24 Percent

Aqueous Streams: The two major aqueous waste streams in the Kosovo Gasification Plant are:

- Gasification section (quenched ash) wastewater, which is a combination of:
    - ash quench water,
    - coal bunker vent gas scrubber blowdown, and
    - ash lock vent gas scrubber blowdown; and
- Phenosolvan wastewater.

Water quality parameters and concentration data for anions and polynuclear aromatics (PNA's) are presented in Table 8.

Gasification section wastewaters contain a variety of pollutants including components leached from the ash or scrubbed from the coal bunker or ash lock vents and components which enter the system along with the ash quench and scrubber makeup water streams. The gasification wastewater has a high pH (due to the alkaline nature of the Kosovo ash) and significant concentrations of dissolved and suspended solids. Other components present (e.g., phenols, NH_3) indicate that at least a portion of the makeup water used in these systems was derived from process condensate. The presence of phenols and NH_3 in the ash lock vent gases tends to confirm this hypothesis since it would not be expected that phenols would be present in any of the other process streams entering the Kosovo ash lock system. The sulfur species detected in these wastewaters were present primarily in the form of sulfate.

TABLE 8. KOSOVO AQUEOUS STREAM DATA

PLANT SECTION:	**GAS PRODUCTION**	**PHENOSOLVAN**	
SAMPLE POINT:	12.3 Quenched Ash Wastewater	14.0 Phenolic Water	14.11 Phenosolvan Wastewater
Design Flow Rate (m^3/gasifier-hr)	3.0	>13	13
pH	0.1 - 12.1	9.2	9.6
Temperature (°C)	-	60	33
Solids Analysis (mg/L)			
Total Solids	10,900	2,320	1,350
Suspended Solids	8,760	150	1,160
Dissolved Solids	2,100	1,170	190
Water Quality Paramters			
COD (as mg O_2/L)	1,460	18,900	7,910
Permanganate (mg/L)	8,060	14.2	4,040
BOD_5 (as mg O_2/L)	90	9,030	2,350
Aqueous Composition Data (mg/L)			
TOC	-	4,970	1,470
Total Phenols	-	2,120	230
Volatile Phenols	0.17	-	130
Free Ammonia	Tr	3,510	Tr
Fixed Ammonia	1.9	250	205
Cyanide	0.01	<1	0.019
Nitrites	0.40	-	Tr
Nitrates	4.8	<1	11.4
Pyridines	-	142	-
Chlorides	28	-	60
Fluorides	0.91	-	Tr
Total Sulfur	-	-	84
Sulfites	Tr	-	-
Sulfates	495	-	110
Sulfides	Tr	-	-
Thiocyanates	0.026	<75	<75
Thiosulfates	Tr	-	Tr
PNA Analysis (mg/L)			
Benz(a)anthracene	-	0.92	NF
7,12-dimethylbenz(a)anthracene	-	0.23	NF
Benzo(a)fluroanthrene	-	0.68	NF
Benzo(a)pyrene	-	0.19	NF
3-methylcholanthrene	-	<0.004	NF
Dibenz(a,h)anthracene	-	0.02	NF
252 Group (as BaP)	-	1.26	0.19

Tr = Trace
NF = Not Found
- = Not Analyzed

The Phenosolvan wastewater stream data presented in Table 8 indicates that a significant reduction in the organic pollutant loading is achieved in the Phenosolvan section. As expected, the phenol level was reduced significantly (by approximately 90 percent) by treatment in this section. It should also be noted that the concentrations of several significant PNA's were reduced to undetectable levels. The fate of the PNA's was not confirmed since no sample of the by-product phenol was obtained. Presumably this by-product stream was the vehicle by which the PNA's present in the inlet water left the unit.

Although a significant portion of the phenolic material was removed from the inlet water by the Phenosolvan unit, a significant amount of organic matter remained in the discharge. This assertion is supported by the following data from Table 8:

- TOC in outlet water - 1,470 mg/L.
- Phenols in outlet water - 230 mg/L.
- Volatile phenols in outlet water - 130 mg/L.

The level of volatile phenols in the outlet water significantly exceeds the DMEG for aqueous discharges (DS Total Phenol = 2.6E04). Since the composition of the unextracted TOC has not yet been determined, no realistic assessment has been made of the characteristics of the bulk of this material. However, in laboratory tests, a relatively large fraction of the inlet TOC (30 percent) remains in the wastewater after extraction in the laboratory with diethyl ether and methylene chloride at pH values of 1 and 12 (Ref. 6).

Solid Streams: Solid phase analytical results are summarized in Table 9. The data shown for the dried coal are based upon an average of approximately 40 different spot samples taken over a several month period. The ash values shown are averages of approximately 20 different samples taken over the same period.

On the average, very high carbon conversion levels were achieved (approximately 99 percent) in the Kosovo Lurgi gasifiers. This is expected for a highly reactive coal such as the lignite being processed at Kosovo. The ash from the gasifiers (after quenching) has a positive heating value, but would not be classified as ignitable and, therefore, would not require special handling in accordance with applicable RCRA criteria for ignitable wastes.

Heavy tar is another solid waste stream produced in the Kosovo gasification facility. Because of the high heating value of this stream as well as the likely presence of highly toxic organic materials, such as phenols and PNA's, this stream would probably be consumed in an on-site steam/power boiler or incinerator in the U.S. At Kosovo, this stream is landfilled.

TABLE 9. KOSOVO SOLID STREAM DATA

PLANT SECTION:	GAS PRODUCTION			TAR SEPARATION
SAMPLE POINT:	2.0	12.1	12.2	13.8
	Dried Coal	Dry Gasifier Ash	Wet Gasifier Ash	Heavy Tar
Ultimate Analysis (wt. %)				
Moisture	20	2.1	not analyzed	(moisture free analysis)
Ash	14	94		6.6
Carbon	45	1.7		56.0
Sulfur	0.89	0.15		0.33
Hydrogen	3.5	0.25		7.6
Nitrogen	1.1	0.03		0.87
Oxygen	16	2.3		28.6
Chlorine	0.01	0.04		-
Proximate Analysis (wt. %)				
Moisture	24	2.1	34	not analyzed
Ash	14	94	59	
Volatile	36	6.5	6.0	
Fixed Carbon	27	-	1.3	
CO_2	2.3	-	5.7	
Total Sulfur	1.2	0.15	0.09	
Free Sulfur	0.35	-	0.02	
Hydrogen	3.4	-	0.38	
Nitrogen/Oxygen	17	-	4.2	
Chlorine	0.01	-	-	
Heating Values (kcal/kg)				
Proximate HHV	3900	27.8	-	-
Proximate LHV	3700	-	-	-
Ultimate HHV	4100	-	-	6340
Specific Gravity	0.538	-	-	-

- = No Data Available

Product and By-Product Streams: The compositions of the products and by-products will affect their final uses and their resulting environmental impacts. Data for the crude and clean product gases are presented in Tables 2 and 3. Comparing the compositions of these streams indicates that the Rectisol unit has removed almost all of the acid gases (CO_2, H_2S, and NH_3) from the product gas.

Chemical analysis data for Kosovo by-products are shown in Table 10. Table 11 presents a comparison of some ultimate analysis data for the feed coal, heavy tar, and liquid by-products. Table 11 indicates that the sulfur contents of the liquid by-products become progressively higher in the "lighter" fractions. In contrast, the trend in the nitrogen values is reversed. These data indicate that heavy hydrocarbon by-products similar to those generated at Kosovo, could be used to satisfy some of the on-site fuel needs (e.g., for steam generation) of a U.S. Lurgi plant without an FGD unit if SO_2 emissions standards consistent with those for large fossil fuel fired steam generators were applicable.

Trace Elements: The trace element concentrations in a number of the plant's key feed, product, by-product, and waste streams were determined to establish whether any of these streams contained elements at concentration levels of concern. In addition, trace element leachabilities were evaluated for the gasifier ash to determine whether this material would be classified as an RCRA hazardous waste. Trace element concentration data are summarized in Tables 12 through 14. These data include both SSMS results, which provide a semiquantitative estimate of trace element concentrations on a broad screening basis, and AA results, which provide more accurate estimates of the concentrations of 15 selected elements. The elements selected for AA analysis were those which were indicated to be present at levels of potential concern by the SSMS results or through previous experience with gasification process waste streams.

The levels of trace elements in the discharge from the LP Coal Lock Vent shown in Table 13 are of particular interest. The concentration of arsenic ($1,700\ \mu g/m^3$) is 850 times its DMEG. Other elements in the LP Coal Lock Vent whose concentration exceeds their DMEG values are chromium (DS = 2.7E02), nickel (DS = 7.8E00), cadmium (DS = 2.7E00), beryllium (DS = 2.0E00), and mercury (DS = 1.1E00). With the possible exception of arsenic, these elements are probably being transported in the coal dust which is contained in the discharge. A significant level of mercury was found in the Phenolic water (Table 13). This value (0.14 mg/L) is 14 times its DMEG for aqueous discharge.

The completion of trace element balances were outside the scope of the Phase II effort. However, rough calculations of trace element distributions were performed to provide some insight into the behavior of trace elements in a Lurgi gasification system. These results are included in Table 13. Most of the recovered trace elements which entered the gasifier with the

TABLE 10. CHEMICAL AND PHYSICAL DATA FOR KOSOVO BY-PRODUCTS

By-Product:	Light Tar	Medium Oil	Naphtha
Specific Gravity (g/cm^3)	1.06	0.97	0.85
Higher Heating Value (kcal/kg)	8910	9500	9940
Lower Heating Value (kcal/kg)	8280	9400	8925
Ultimate Analysis (wt %)			
Carbon	82	82	86
Hydrogen	8.4	8.9	9.9
Nitrogen	1.3	1.00	0.18
Sulfur	0.49	0.83	2.2
Ash	0.22	0.03	----
Chlorine	----	----	----
Oxygen (difference)	7.8	8.2	2.2
Moisure Content (wt %)	1.1	0.8	----
PNA Analysis (mg/kg)			
Benz(a)anthracene	490	160	NF
7,12-dimethylbenz(a)anthracene	1100	62	NF
Benzo(b)fluoroanthrene	310	120	NF
Benzo(a)pyrene	210	68	NF
3-methylcholanthrene	26	NF	NF
Dibenz(a,h)anthracene	23	6.6	NF
252 Group (as BaP)	950	280	NF

NF = not found
- = no data available

TABLE 11. COMPARISON OF ULTIMATE ANALYSIS DATA FOR SELECTED KOSOVO SOLIDS AND BY-PRODUCTS

Component	Dried Coal	Heavy Tar*	Light Tar	Medium Oil	Naphtha
C	45	56	82	82	86
H	3.5	7.6	8.4	8.9	9.9
N	1.1	0.87	1.3	1.0	0.2
S	0.89	0.33	0.49	0.83	2.2
Ash	14	6.6	0.22	0.03	-
O	16	29	7.8	8.2	2.1
Moisture	20	-	1.1	0.8	-
HHV**	16.3	26.5	37.3	40.0	41.6
SO_2***	1090	250	260	420	1060

* Moisture Free Analysis
** Higher Heating Value expressed as KJ/g.
*** Expressed as ng/J assuming 100% conversion of S to SO_2.

NOTE-SO_2 Emission Limitations for Large Fossil Fuel Fired Steam Generators (40 CFR 60D):

Coal and Solid Fuels - 520 ng/J (1.2 lb/10^6 Btu)
Liquid Fuels - 340 ng/J (0.8 lb/10^6 Btu)

TABLE 12. A SURVEY OF TRACE ELEMENTS IN KOSOVO STREAMS ANALYZED BY SSMS

SAMPLE POINT:	2.0	12.1	12.2	13.2	14.11
Trace Element	Dried Coal (mg/kg)	Dry Gasifier Ash (mg/kg)	Wet Gasifier Ash (mg/kg)	Medium Oil (mg/L)	Phenosolvan Wastewater (mg/L)
Ag	NF	NF	NF	NF	NF
Al	>1000	>1000	—	0.09	0.1
As	2	62	—	0.4	0.02
B	21	190	630	0.07	0.1
Ba	110	>1000	1670	0.09	0.05
Be	NF	4	NF	NF	NF
Bi	NF	NF	NF	0.01	NF
Br	2	17	—	NF	0.009
Ca	>1000	>1000	—	5	6
Cd	0.4	NF	1.2	0.01	NF
Ce	3	29	—	0.003	NF
Cl	32	45	—	0.008	0.08
Co	0.4	4	15	0.004	0.003
Cr	11	2	240	0.02	0.005
Cs	0.1	3	—	NF	NF
Cu	8	27	76	0.3	0.03
Dy	NF	2	—	NF	NF
Er	NF	0.5	—	NF	NF
Eu	<0.3	1	—	NF	NF
F	2	≈710	—	≈0.03	≈0.02
Fe	>1000	>1000	—	2	0.5
Ga	2	17	37	NF	NF
Gd	NF	2	—	NF	NF
Ge	0.1	0.3	—	NF	0.03
Ho	NF	0.6	—	NF	NF
I	0.5	2	—	NF	0.02
K	>1000	>1000	—	0.3	1
La	2	21	NF	NF	NF
Li	1	28	—	0.001	0.003
Lu	NF	NF	—	<0.004	NF
Mg	>1000	>1000	—	>10	2
Mn	230	>1000	2700	0.02	0.01
Mo	6	6	30	0.005	NF
Na	>1000	>1000	—	0.1	4
Nb	3	10	—	NF	NF
Nd	0.8	10	—	NF	NF
Ni	23	180	180	0.03	0.08
Np	NF	10	—	NF	NF
P	780	>1000	—	0.1	0.08
Pb	2	9	27	0.09	0.07
Pr	0.9	3	—	NF	NF
Rb	5	35	—	NF	NF
S	>1000	420	—	0.6	>10
Sb	NF	2	NF	NF	NF
Sc	1	12	20	<0.001	<0.005
Se	0.6	≤ 1	—	0.02	0.03
Si	>1000	>1000	—	2	1
Sm	1	9	—	NF	NF
Sn	0.3	0.8	NF	0.008	0.009
Sr	91	320	4100	0.008	0.02
Tb	NF	0.4	—	NF	NF
Te	0.4	< 1	—	NF	NF
Th	< 2	9	—	<0.02	<0.04
Ti	660	>1000	2300	0.09	0.02
U	< 2	2	—	0.07	<0.03
V	8	67	140	0.01	0.003
Y	2	17	39	0.003	<0.03
Zn	1	33	56	0.3	0.7
Zr	6	33	180	<0.003	0.02

NF = not found
— = no data available

TABLE 13. TRACE ELEMENTS IN KEY KOSOVO STREAMS ANALYZED BY ATOMIC ABSORPTION SPECTROMETRY

SAMPLE POINT:	SOLIDS					
	2.0 Dried Coal		12.1 Dry Gasifier Ash		13.8 Heavy Tar	
Trace Element	Concentration (mg/Kg)	Mass Flow (g/hr)	Concentration (mg/Kg)	Mass Flow (g/hr)	Concentration (mg/Kg)	Mass Flow (g/hr)
As	59	940	75	200	16	1.6
Be	1.0	16	2.5	6.8	0.29	0.029
Cd	4.0	64	69	190	3.7	0.37
Ce	3.4	54	17	46	1.5	0.15
Cr	87	1400	180	490	30	3.0
Cu	43	690	40	110	6.0	0.60
Hg	0.74	12	0.30	0.82	0.64	0.064
Mo	6.4	100	8.9	24	0.85	0.085
Ni	150	2400	320	860	21	2.1
Pb	8.2	130	52	140	64	6.4
Sb	NF	NF	NF	NF	3.9	0.39
Se	20	320	24	65	2.6	0.26
Sr	190	3000	370	1000	41	4.1
Tl	NF	NF	NF	NF	NF	NF
V	14	220	100	270	5.7	0.57
Zn	140	2200	2.1	5.7	98	9.8

NF - below detection limits

(Continued)

TABLE 13 (Continued). TRACE ELEMENTS IN KEY KOSOVO STREAMS ANALYZED BY ATOMIC ABSORPTION SPECTROMETRY

SAMPLE POINT:	LIQUID BY-PRODUCT						WATER	
	15.1 Light Tar		15.2 Medium Oil		15.3 Naphtha		14.0 Phenosolvan Inlet Water	
Trace Element	Concentration (mg/kg)	Mass Flow (g/hr)	Concentration (mg/kg)	Mass Flow (g/hr)	Concentration (mg/kg)	Mass Flow (g/hr)	Concentration (mg/L)	Mass FLow (g/hr)
As	1.7E+01	6.8E 00	2.0E 00	5.0E-01	5.5E-01	8.5E 02	1.0E-01	1.3E 00
Be	9.0E-02	3.6E-02	NF	NF	1.8E-03	2.7E-04	NF	NF
Cd	6.6E-01	2.64E-01	7.7E-02	1.9E-02	8.0E-04	1.2E-04	1.4E-03	1.8E-02
Co	NF	NF	2.0E-01	4.5E-02	5.0E-03	7.7E-04	NF	NF
Cr	3.0E 00	1.2E 00	4.0E 00	1.0E 00	1.0E 01	1.5E 02	2.3E-02	3.0E-01
Cu	1.6E+01	6.4E 00	1.1E 00	2.8E-01	1.5E-01	2.4E-02	1.1E-02	1.4E-01
Hg	NF	NF	2.0E-01	5.2E-02	1.3E-01	2.0E-02	1.4E-01	8.2E 00
Mo	NF	NF	1.9E-01	4.8E-02	9.0E-03	1.4E-03	NF	NF
Ni	9.0E-00	3.6E 00	NF	NF	1.4E-01	2.1E-02	1.3E-02	1.7E-01
Pb	6.8E 00	2.7E 00	1.4E 00	3.5E-01	6.4E-02	9.8E-03	1.4E-02	1.8E-01
Sb	NF	NF	NF	NF	1.2E-02	1.9E-03	NF	NF
Se	1.6E 00	6.4E-01	1.9E 00	4.8E-01	7.3E-01	1.1E-01	5.0E-02	6.5E-01
Sr	2.0E+01	8.0E 00	8.6E 00	2.2E 00	NF	NF	1.0E-01	1.3E 00
Tl	NF	NF	NF	NF	NF	NF	NF	NF
V	NF	NF	NF	NF	NF	NF	NF	NF
Zn	2.8E+01	1.1E+01	1.5E+01	3.8E 00	1.4E-01	2.1E-02	2.8E-01	3.6E 00

NF = Not Found (below detection limits)

(Continued)

TABLE 13 (Continued). TRACE ELEMENTS IN KEY KOSOVO STREAMS ANALYZED BY ATOMIC ABSORPTION SPECTROMETRY

	GASES				
SAMPLE POINT:	3.2 Low Pressure Coal Lock Vent		20.1 Combined Gas to Flare		
Trace Element	Concentration (mg/L)	Mass Flow (g/hr)	Concentration (mg/L)	Mass Flow (g/hr)	Percentage of Amount Found in Dried Coal Accounted For in the Streams Listed in this Table
As	1.7E-03	3.6E-02	1.9E-06	2.5E-03	22
Be	4.0E-06	8.4E-05	NF	NF	43
Cd	2.7E-05	5.7E-04	2.4E-07	3.2E-04	298
Ce	4.9E-06	1.0E-04	1.7E-07	2.3E-04	85
Cr	2.7E-04	5.7E-03	NF	NF	35
Cu	1.8E-04	3.8E-03	5.8E-06	7.7E-03	17
Hg	5.3E-05	1.1E-03	NF	NF	23
Mo	4.5E-05	9.5E-04	NF	NF	24
Ni	1.2E-04	2.5E-03	7.5E-06	1.0E-02	36
Pb	7.2E-05	1.5E-03	1.0E-06	1.3E-03	115
Sb	NF	NF	NF	NF	-
Se	NQ	NQ	7.2E-06	9.6E-03	21
Sr	6.1E-04	1.3E-02	4.4E-06	5.9E-03	34
Tl	NF	NF	NF	NF	-
V	9.0E-06	1.9E-04	NF	NF	123
Zn	1.6E-03	3.4E-02	3.1E-05	4.1E-02	1.5

NF = below detection limits
NQ = present but not quantifiable

TABLE 14. TRACE ELEMENTS IN KOSOVO ASH LEACHATES ANALYZED BY SSMS

	RCRA LEACHATE (Acid)		ASTM LEACHATE (Neutral)	
Trace Element	Composition (mg/L)	D.S. Value	Composition (mg/L)	D.S. Value
Al	0.01	1.30E-04	2	2.50E-02
As	≤0.004	≤1.60E02	0.01	4.00E-02
B	0.09	1.91E-03	0.1	2.12E-03
Ba	3	6.00E-01	0.05	1.00E-02
Be	NF	-	NF	-
Bi	NF	-	NF	-
Br	≤0.008	0.0	0.4	0.0
Cd	NF	-	NF	-
Ce	NF	-	NF	-
Cl	0.05	3.84E-05	0.7	5.40E-04
Co	≤0.001	≤1.33E-03	≤0.007	≤9.33E-03
Cr	0.3	1.20E 00	0.5	2.00E 00
Cs	0.004	3.33E-06	NF	-
Cu	0.01	2.00E-03	0.03	6.00E-03
Dy	NF	-	NF	-
Er	NF	-	NF	-
Eu	NF	-	NF	-
F	0.8	2.10E-02	7	1.84E-01
Fe	10	6.70E 00	0.1	6.70E-02
Ga	NF	-	0.02	2.70E-04
Gd	NF	-	NF	-
Ge	≤0.001	<1.20E-04	0.01	1.20E-03
Ho	NF	-	NF	-
I	NF	-	0.005	0.0
La	NF	-	NF	-
Li	0.03	9.10E-02	0.07	2.12E-01
Mg	2	2.22E-02	NF	-
Mn	0.001	4.00E-03	0.02	8.70E-02
Mo	0.1	1.33E-03	0.05	6.70E-04
Na	>2	>2.50E-03	NF	-
Nb	NF	-	0.006	1.81E-05
Ni	0.04	1.73E-01	0.02	8.70E-02
Np	NF	-	NF	-
P	0.02	1.33E-02	0.2	1.33E-02
Pb	0.008	3.20E-02	0.07	2.80E-01
Pr	NF	-	NF	-
Rb	0.04	2.22E-05	0.09	5.00E-05
S	>6	0.0	NF	-
Sb	≤0.002	≤2.70E-04	NF	-
Sc	≤0.001	≤1.30E-06	≤0.003	≤3.74E-06
Se	0.01	2.00E-01	0.007	1.40E-01
Si	8	5.33E-02	7	4.70-E02
Sm	NF	-	NF	-
Sn	≤0.001	0.0	NF	-
Sr	4	8.70E-02	0.3	6.52E-03
Tb	NF	-	NF	-
Te	NF	-	NF	-
Th	<0.008	<1.30E-03	<0.04	<6.34E-03
Ti	0.01	1.11E-04	0.02	2.22E-04
U	<0.007	<1.20E-04	<0.03	<5.00E-04
V	0.07	2.80E-02	0.004	1.60E-03
Y	0.008	5.33E-04	NF	-
Zn	0.05	2.00E-03	0.08	3.20E-03
Zr	≤0.006	≤8.00E-05	NF	-

NF = Not Found

feed coal were found in the gasifier ash. The recovery values shown are based upon the use of plant design flow data for the feed, by-product, and waste streams considered. The only trace elements found in any significiant concentrations in streams other than the dry gasifier ash are antimony and lead (in the heavy tar), and copper (in the by-product naphtha). Very poor calculated recoveries were obtained for most of the trace elements (on the order of 20 to 40 percent). Zinc recoveries were particularly poor, with less than 5 percent of the coal input zinc accounted for. These poor recovery values are probably the result of several factors including: actual stream flow measurements were not obtained for many of the streams, time phased sampling was not attempted, and a statistically significant data base was not obtained.

The largest solid waste stream generated in a Lurgi gasification plant is quenched gasifier ash. In order to determine the leaching characteristics of this material and to predict its classification under RCRA guidelines, a series of leaching studies were conducted. The results of these tests, which are reported in Table 14, indicate that no trace elements were present in the ash leachate in sufficient concentrations which would cause this material to be classified as hazardous.

A Comparison of Discharge Streams Plant Wide: TWDS values for all major discharge streams - aqueous, gaseous, and solid - are shown in Figure 18. Attention is called to the flow rate units: liters per gasifier hour - aqueous streams; cubic meters per gasifier hour - gaseous streams; and kilograms per gasifier hour - solid streams. These are the units of the DMEGS used. Figure 18 shows the streams prioritized in each discharge medium according to their TWDS values.

Mass Balances for Key Species: Figure 19 summarizes the results of mass balance calculations for carbon, sulfur, and nitrogen species in the Kosovo plant. The amount of carbon found in key Kosovo solid, liquid, and gaseous streams, expressed as a percentage of the carbon entering the gasifier in the dried coal indicates that the majority of the carbon entering the system with the dried coal leaves in gaseous streams. It is significant that there is almost as much carbon (mainly as CO_2) in the H_2S-rich waste gas flare feed stream (88 vol. % CO_2) as there is in the CO_2-rich waste gas stream (94 vol. % CO_2). Small quantities of the inlet carbon ends up in the gasifier ash (0.7%), aqueous wastewaters (0.3%), and the remaining gaseous discharge streams (excluding the CO_2-rich waste gas stream).

Most of the sulfur leaves the plant in the H_2S-rich waste gas stream. Of the remaining sulfur, the majority appears in the by-products - naphtha (1.5%), medium oil (1.1%), and light tar (1.1%) - and the ammonia stripper vent (3.7%). A small percentage is discharged in the ash (1.3%), heavy tar (0.2%), and aqueous wastewaters (0.9%). The relatively poor accountability of the sulfur balance is probably due to variations in the input coal sulfur content, variations in flow rate measurements, and the lack of time-phased sampling.

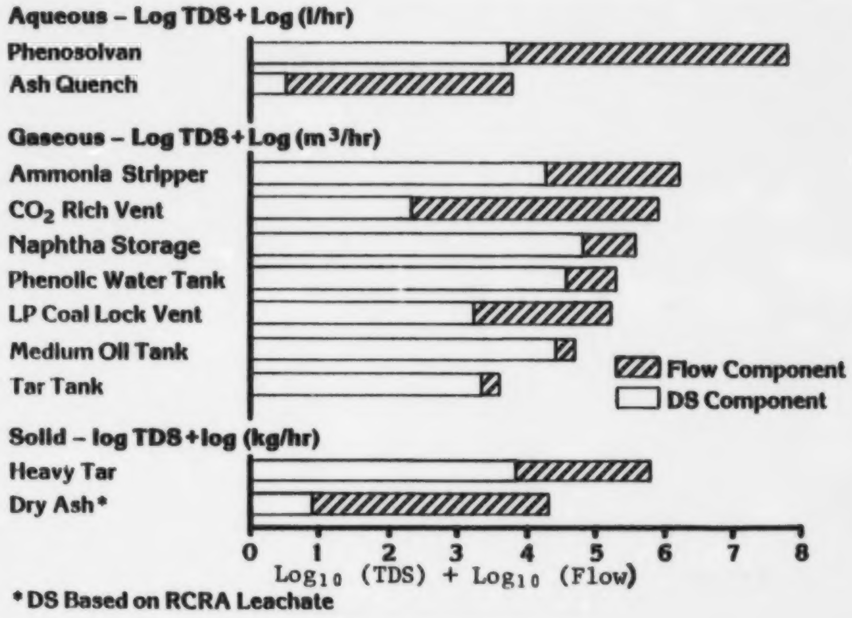


Figure 18. Total weighted discharge severity of uncontrolled Kosovo discharge streams.

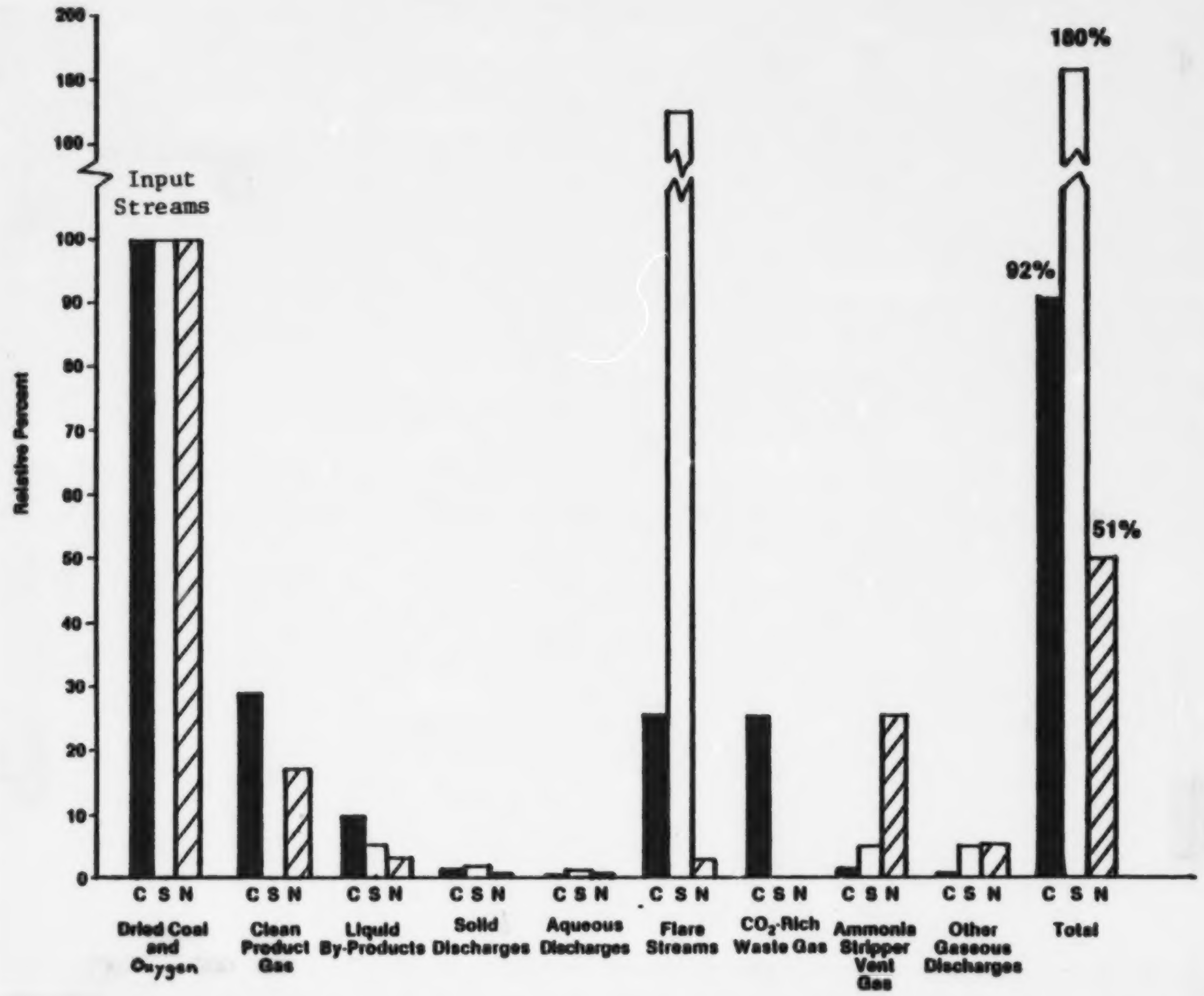


Figure 19. Summary of Carbon, Sulfur, and Nitrogen Mass Balance Results for the Kosovo Plant

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Nitrogen entering in the dried coal and oxygen feed streams is converted primarily to ammonia, hydrogen cyanide, a number of organic nitrogen compounds, and N_2. Most of this nitrogen appears in gaseous discharge streams. A large percentage is discharged in the ammonia stripper vent (which contains 41.8 vol. % NH_3 on a dry basis).

Summary and Conclusions: The Kosovo Phase II data has corroborated substantially the indications from the Phase I test results and has also added significant new information about the aqueous and solid discharges from the Kosovo plant. It has also provided significant information about trace pollutants, both organic and inorganic. The following are some of the more salient findings:

- All process units studied have a significant potential for polluting the environment.
- The highest priority streams in each medium are:
  - H_2S-rich waste gas,
  - Phenosolvan wastewater, and
  - heavy tar.
- The CO_2-rich waste gas may contain significant levels of nonmethane hydrocarbons and mercaptans.
- PNA's make a significant contribution to the discharge severity (DS) of tar-bearing streams (e.g., LP Coal Lock vent and heavy tar).

  The severity of the coal lock vent discharge is increased significantly by the contribution of PNA's in the tar aerosols.
- Benzo(a)pyrene and 7,12-Dimethylbenz(a)anthracene are the two most significant (highest D.S. values) pollutants in Kosovo tar.
- Trace elements appear to be less significant than trace organics as pollutants in organic containing streams.
- Ash leaching problems appear to be of low concern. Concentrations of all trace elements were at least an order of magnitude lower in the RCRA leach test results than those levels specified in the EP toxicity test.
- After Phenosolvan treatment, the treated process condensate contained undetectable levels of PNA's, but high residual organic material concentrations and high solids concentrations.

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AMBIENT AIR DOWNWIND OF THE KOSOVO GASIFICATION COMPLEX: A COMPENDIUM

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ABSTRACT

In an attempt to obtain environmental impact data for a commercial scale coal gasification facility the Environmental Sciences Research Laboratory-RTP (ESRL-RTP) Aerosol Research Branch, conducted a 16-d continuous ambient air study in the Region Kosovo, Yugoslavia. Five sampling sites were established around and ≈2 km outside the fence line of the Kosovo medium BTU Lurgi gasification complex.

Organics in total particulate matter; total and fine particle mass, inorganics, and elemental species; trace metal in size-fractionated particles; and vapor phase organics were determined. Physical and chemical analyses were carried out on particulate matter using gravimetric analysis, ion chromatography, and scanning electron microscopy. Elemental analysis was done using the inductively coupled argon plasma emission technique, proton-induced X-ray emission, and combustion analysis. Both particle catches and vapors trapped on Tenax resins were subjected to organic analysis using gas chromatography. The chromatographic fractions were identified and quantified using flame ionization detection, sulfur and nitrogen specific detectors, and mass spectrometry. A comprehensive quality assurance and quality control program was implemented to ensure the validity of the samples collected and analyzed.

A number of United States and Yugoslavian laboratories participated in the ambient air sampling and analysis phases of this study. This paper is a compendium of the major results and conclusions obtained by the participant laboratories.

INTRODUCTION

The Environmental Sciences Research Laboratory-RTP (ESRL-RTP) Aerosol Research Branch conducted an ambient air study near the commercial medium BTU Lurgi coal gasification plant located in the Kosovo Region of Yugoslavia. The objectives of the study were to characterize the ambient aerosols and volatile organic pollutants downwind of the Kosovo complex, to correlate specific pollutants to the gasification plants, and to evaluate the impact of the Lurgi gasification process on the air quality downwind of the Kosovo complex. This study represents Phase III of the Industrial Environmental Research Laboratory-RTP (IERL-RTP) multimedia assessment program at the Kosovo complex.

The Kosovo Industrial Complex (Kombinat Kosovo) consists of a coal processing facility, a coal gasification plant (six Lurgi gasifiers), a fertilizer plant, a steam plant, a 790 MW lignite burning power plant, and a gasification process by-product storage area. Major activities outside the complex are lignite coal mining, lignite ash disposal (piles), and farming. Forty-eight trains (27 diesel and 21 steam) pass along the southern edge of the Kosovo complex daily. Several improved analytical techniques and procedures were developed by Radian Corporation[1,2,3] and by the Oak Ridge National Laboratory[4,5,6] in anticipation of difficulty in differentiating the complex sources in the area.

SAMPLING STRATEGY

Five sampling sites were located around and ≈2 km outside the fence line of the Kosovo complex. Using the stack of the steam plant as a center reference point and Yugoslav wind direction data for the month of May (average winds from Northeast), the sampling stations were deployed in a manner indicative of prevailing upwind, downwind, and crosswind locations (see Figure 1).

Each sampling station was equipped to collect total suspended particulate (TSP) matter for organic analysis; total (<15 μm) and fine (<2.0 μm) particles for gravimetric, inorganic, and elemental analysis; size-fractionated particles for elemental analysis; and organic vapors. The sample collection equipment at each station consisted of:

1. one 24 h HiVol sampler (1.1 m^3/min) using a 265 mm diameter Gelman Microquartz filter and a HiVol motor exhaust filtration system[7];
2. one 24 h Tenax vapor trap system[8] (4 l/min) which taps into the post-filter section of the HiVol sampling head;
3. one 6 h LoVol sampler (28 l/min) using two 47 mm diameter Gelman Microquartz filters, one total (<15 μm) and one fine (<2.0 μm), preceeded by a Southern Research Institute - Cyclone II[9];
4. one 6 h modified Battelle cascade impactor[10] (1 l/min);
5. one 7 d time-phased aerosol sampler[10] (≈2 l/min); and
6. one Sears 3 kW gasoline electric power generator positioned 40 m downwind of the sampling equipment.

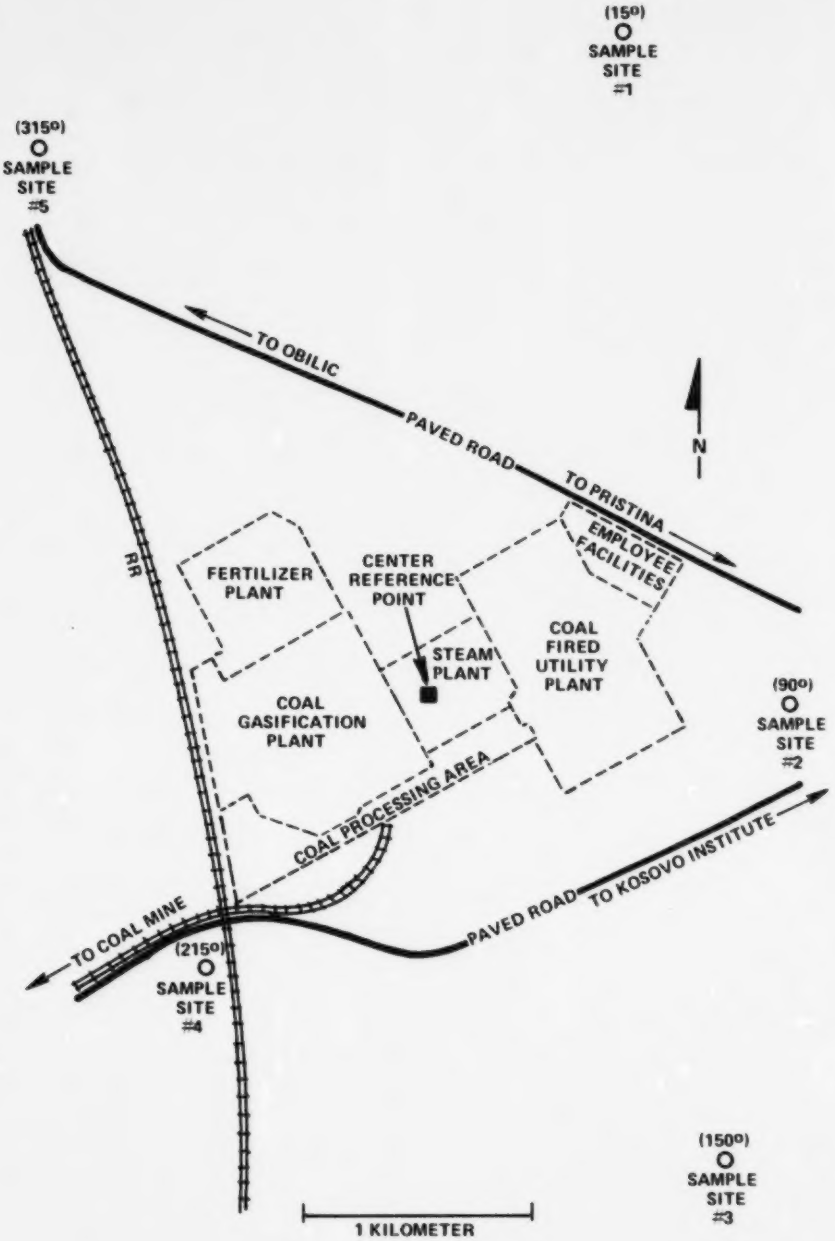
(15°)
SAMPLE SITE #1
(315°)
SAMPLE SITE #5
TO OBILIC
PAVED ROAD
TO PRISTINA
N
EMPLOYEE FACILITIES
RR
FERTILIZER PLANT
CENTER REFERENCE POINT
STEAM PLANT
COAL FIRED UTILITY PLANT
(90°)
SAMPLE SITE #2
COAL GASIFICATION PLANT
COAL PROCESSING AREA
TO COAL MINE
PAVED ROAD
TO KOSOVO INSTITUTE
(215°)
SAMPLE SITE #4
(150°)
SAMPLE SITE #3
1 KILOMETER

Figure 1. Schematic of the Kosovo complex with the five sampling sites indicated (Reference 1).

Site No. 3 was equipped with a Bendix Aerovane (6 blade) wind speed, wind direction, and time system. Site No. 5 was equipped with a Climatronics meteorological station and a Datel Data Logger II magnetic tape system which recorded wind speed, wind direction, solar flux, barometric pressure, temperature, and time. The meteorological data from Site No. 5 were used to calculate percent downwind values for each site location.[1]

Mass measurements on LoVol filters were made on a Mettler Model ME 30/36 Electronic Microbalance. Quality assurance audits[1] covering sample collection media preparation, equipment calibration and operation, initial and final gravimetric measurements, sample storage and transport, and sample documentation were conducted daily by on-site personnel representing the prime contractor, Radian Corporation. All aspects of sample collection and handling, except quality assurance/quality control, were carried out by Yugoslav personnel under American supervision.

Sampling began at 0000 h on May 14 and ended at 2400 h on May 29, 1979. Approximately 3000 samples were collected during the study. The samples were distributed between several investigators for analysis (see Table 1).

ANALYSIS STRATEGY

The objectives of the analysis program were to analyze the aerosols and vapors collected in the vicinity of the Kosovo complex, and to compare the ambient air results with those obtained from the analysis of Kosovo gasification process emissions and by-product streams. To accomplish these objectives four integrated courses of analysis were followed: (1) physical characterization

Table 1. SAMPLES COLLECTED AND RESPECTIVE RECIPIENTS[a]

ORGANIZATION	HIVOL FILTERS	ORGANIC VAPOR TRAPS	BATTELLE IMPACTOR DISC SETS	STREAKER SAMPLER SLIDES	LOVOL FILTERS	GRAB SAMPLE BOMBS
INEP[b]	42	83	157	6	316	3
RADIAN	23	42			326[c]	
ORNL	22	42				
FSU			161	12		
EPA/GKPB						3
TOTALS	87	167	318	18	642	6

[a] FROM REFERENCE 1.

[b] INEP (INSTITUT ZA PRIMENU NUKLEARNE ENERGIJE, BELGRADE, YUGOSLAVIA).

[c] THE OREGON GRADUATE CENTER RECEIVED TWO SECTIONS FROM EACH LOVOL FILTER IN RADIAN'S POSSESSION.

of the aerosol; (2) carbon speciation of the aerosol; (3) inorganic analysis of the aerosol; and (4) organic analysis of the species in the vapor phase and adsorbed on the aerosol.

The percentage of time that each station was located downwind from the gasification plant was of interest for the purpose of correlating identified chemical species with their source(s). The reduction and analysis of the Climatronics meteorological data indicated that Site No. 4 was the predominant downwind location (≈40%) and that Sites No. 1 and No. 5 were the predominant upwind locations (≈1%). Site No. 3 (≈20%) was an intermediate location. Samples from Sites 1, 3, and 4 received first priority for screening and analysis.

ANALYSIS RESULTS

Physical Analysis

Gravimetric data showed that the ambient aerosol loadings (both <15 μm and <2.0 μm) were significantly greater downwind of the Kosovo complex than upwind (note Figure 2). The increase was greater for the coarse (total minus fine) aerosol fraction than for the fine fraction. The particulate matter collected downwind of the complex appeared to be mineral; only small amounts (<1%) of typically spherical fly ash material were observed. The latter result indicates that the sampling stations were located in areas least affected by the plume of the Kosovo power plant.

Carbon Analysis

Carbon speciation analysis by Huntzicker, et al. (Oregon Graduate Center)[11] showed the coarse aerosol fractions from Site

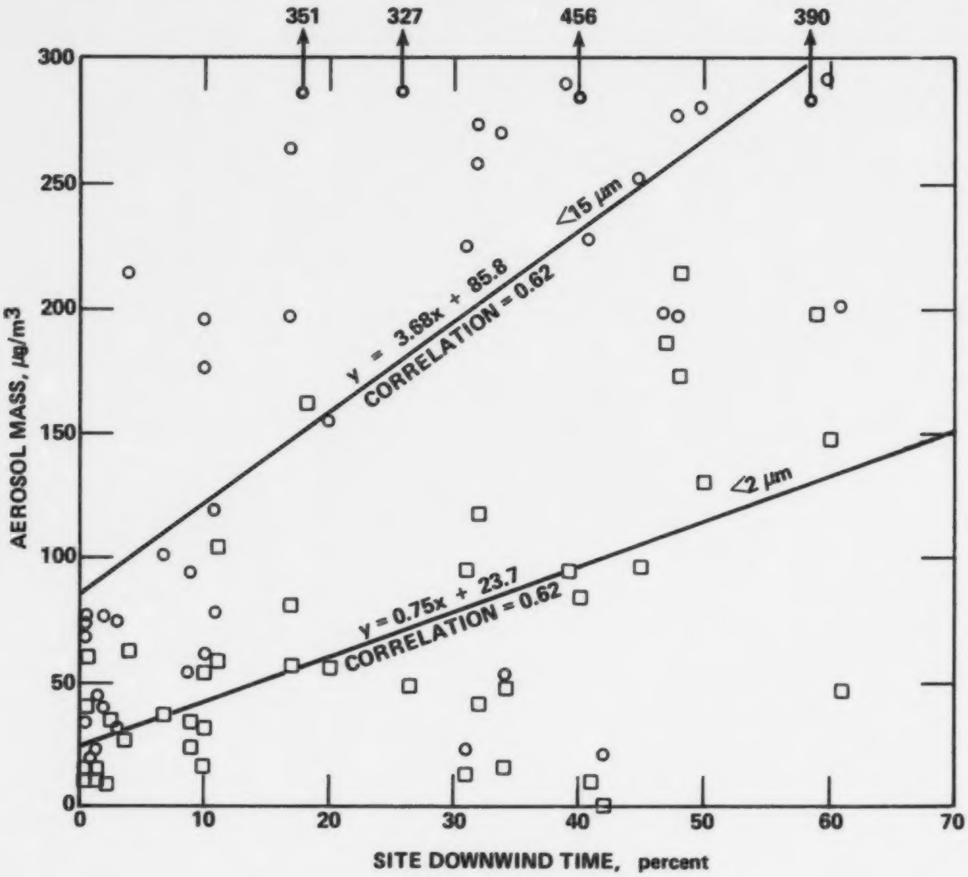

Figure 2. A Plot of the <15 μm and <2.0 μm particle fractions versus percent downwind. The lines are the linear-least-squares plot of the data (Reference 1).

No. 4 (downwind) to exhibit a very strong periodicity in elemental carbon concentration. This peaking always appeared at night. Weaker periodicities were observed for coarse organic carbon and total (<15 μm) carbonate carbon. Site No. 4 also exhibited a daytime peaking trend in organic carbon concentration in the fine aerosol fraction. An explanation for this pattern has not yet been developed. The elemental carbon and organic carbon in the fine fraction were weakly correlated ($r = 0.36$) at Site No. 4, suggesting a multiplicity of sources and poor mixing. At Site No. 5 (upwind), the organic and elemental carbon in the fine fraction were strongly correlated ($r = 0.77$). For all sites and sampling periods, when the percent of time downwind was <5%, the correlation coefficient was 0.63. The latter two results indicate well aged aerosol similar to aerosol sampled at urban U.S. sites. The high concentrations of carbonate carbon (up to 12 $\mu C/m^3$) observed during many of the high mass loading periods suggest blowing coal dust. This is a reasonable assumption in that Kosovo lignite is rich in carbonate.[12] Total carbon analysis data obtained by Radian[1] showed that a higher percentage of carbon was collected downwind of the plant and that the additional carbon was >2.0 μm in diameter. Upwind, ≈70-80% of the carbon was in the <2.0 μm fraction.

Inorganic Analysis

Preliminary data from Boueres, et al. (Florida State University)[13] on the time phase streaker sampler at Site No. 4 showed regular daytime peaking of sulfur and iron as well as lead and zinc. These element pairs are not synchronous but may be related to the peaking seen by Huntzicker, a possibility now being investigated. There are some indications of photochemical activity and sulfur transformation chemistry. However, this inference will remain speculative until more definitive data are obtained through a more detailed analysis of the impactor and streaker data bases.

Figure 3 shows the average background concentration of sulfur at all sites to be on the order of 2 $\mu g/m^3$. With the exception of Site No. 5, all sites show maxima in $[\overline{S}]$ occurring at different times of the day between 1200 and 1800 h. Each maximum of $[\overline{S}]$ appears to be composed of a distinct peak superimposed on a *smooth* (bell shaped) *maximum*. From the wind direction and site position information, we hypothesize that the distinct peak may be associated with direct emission plus rapid heterogeneous transformation within the plume. The other two components (the *background* and the *smooth maximum*) may be associated with homogeneous nucleation, slow heterogeneous reaction, and resuspension of particles deposited in the soil.[14]

Preliminary assessment of the Kosovo samples thus far suggests that most of the observed trace metal aerosol components were derived from sources other than the coal gasification plant. Radian's[1,15] inorganic analyses also show no correlations between concentration and percent downwind from the coal gasification facility for any soluble (Na^+, NH_4^+, NO_3^-, Cl^-, and $SO_4^=$) or elemental species except total carbon (discussed above). Iron, lead, and zinc data analyses are incomplete at this time.

Organic Analysis

The Tenax resin cartridges analyzed by Radian[1] showed organic species in the volatility range from benzene to pyrene. Benzene

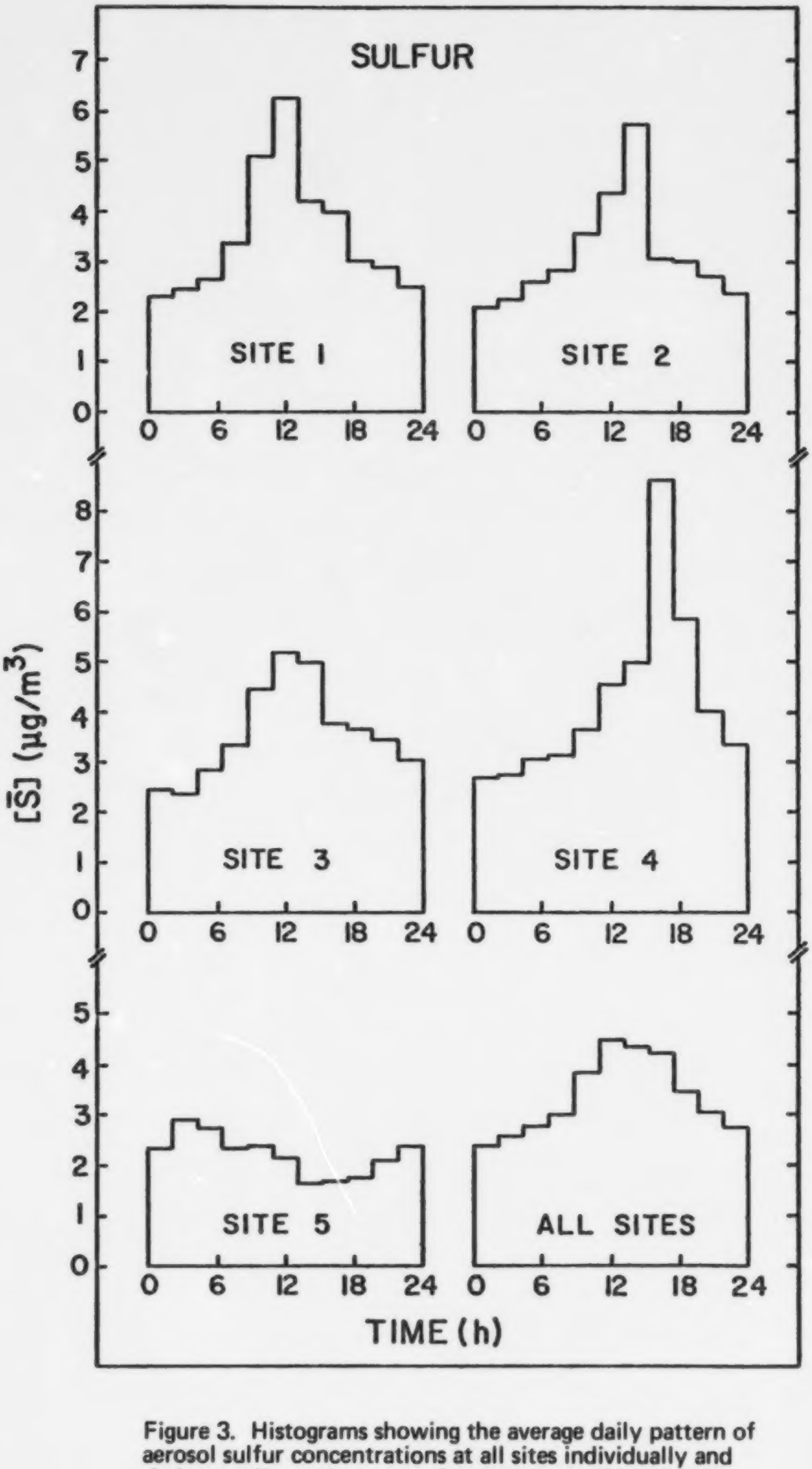

Figure 3. Histograms showing the average daily pattern of aerosol sulfur concentrations at all sites individually and their overall grand average. Plotted are the 2-h averages of [S] for the 15.5 days of sampling (14-26 May 1979) (Reference 14).

and toluene (and possibly other volatile species) experienced breakthrough and were not quantifiable, but xylenes and all heavier compounds were quantitatively collected. There is a clear distinction (with some overlap) between the organic compounds adsorbed on the particulate matter caught on the HiVol filter and in the vapors sorbed on the Tenax resin. The vapors spanned benzene (MW 78) to pyrene (MW 202). The filter samples contained polynuclear aromatic hydrocarbons (PAH's) from naphthalene (MW 128) through the benzopyrene isomeric group (MW 252).

Mass spectrometric analysis of Tenax and filters samples succeeded in tentatively identifying more than 50 organic compounds and isomeric groups in the ambient air downwind of the Kosovo Industrial Complex. The list of identified compounds includes: alkylated benzenes through C_4 substitution, polyaromatic hydrocarbons (PAH's) and alkylated PAH's through benzopyrenes, linear and heterocyclic hydrocarbons, phenols, ketones, alkylated pyridines and quinolines, alkylated thiophenes, and dibenzofuran. Some of the volatile organic compounds detected in the ambient air were identical to some of the compounds found in certain emissions from the coal gasification plant (see Figures 4-7).

Quantification by mass spectrometry and flame ionization detection placed the maximum individual concentrations of naphthalene in the vapor phase and benzopyrene isomer group adsorbed on the particulate matter at 8 $\mu g/m^3$ and 0.08 $\mu g/m^3$, respectively, when extrapolated to 100% downwind. The basis for such an extrapolation is shown in Figure 8. Comparison of measured concentrations with Ambient-Multimedia Environmental Goal (A-MEG)[16] values

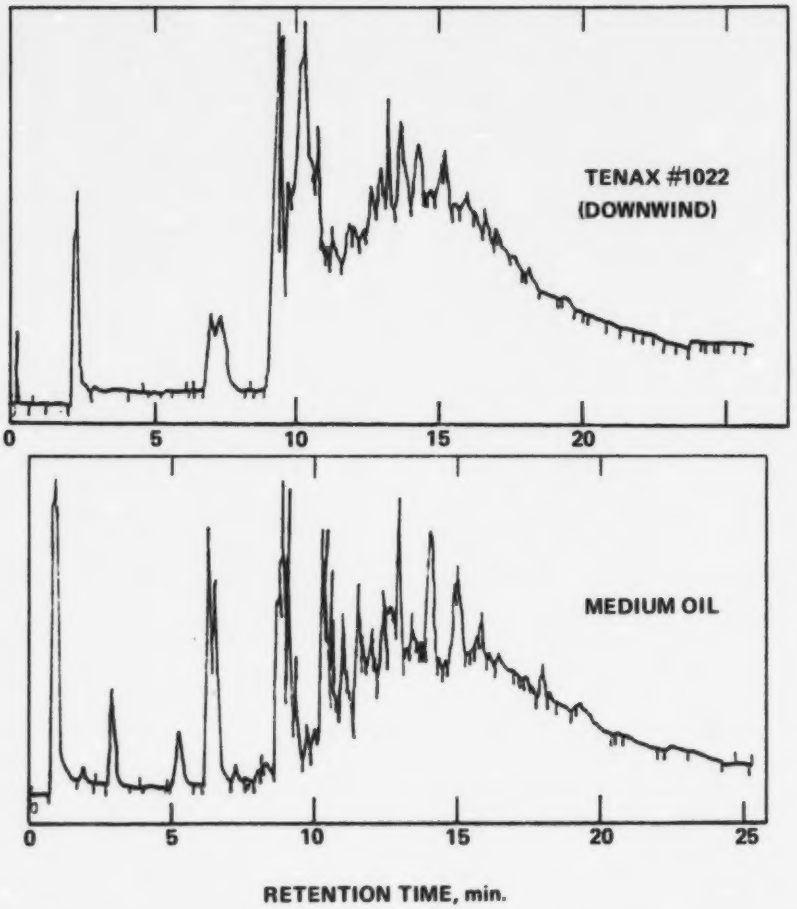

Figure 4. GC-HECD sulfur compound profiles for a downwind Tenax vapor trap extract (#1022, day 6, site #4) and for Kosovo medium oil (Reference 1).

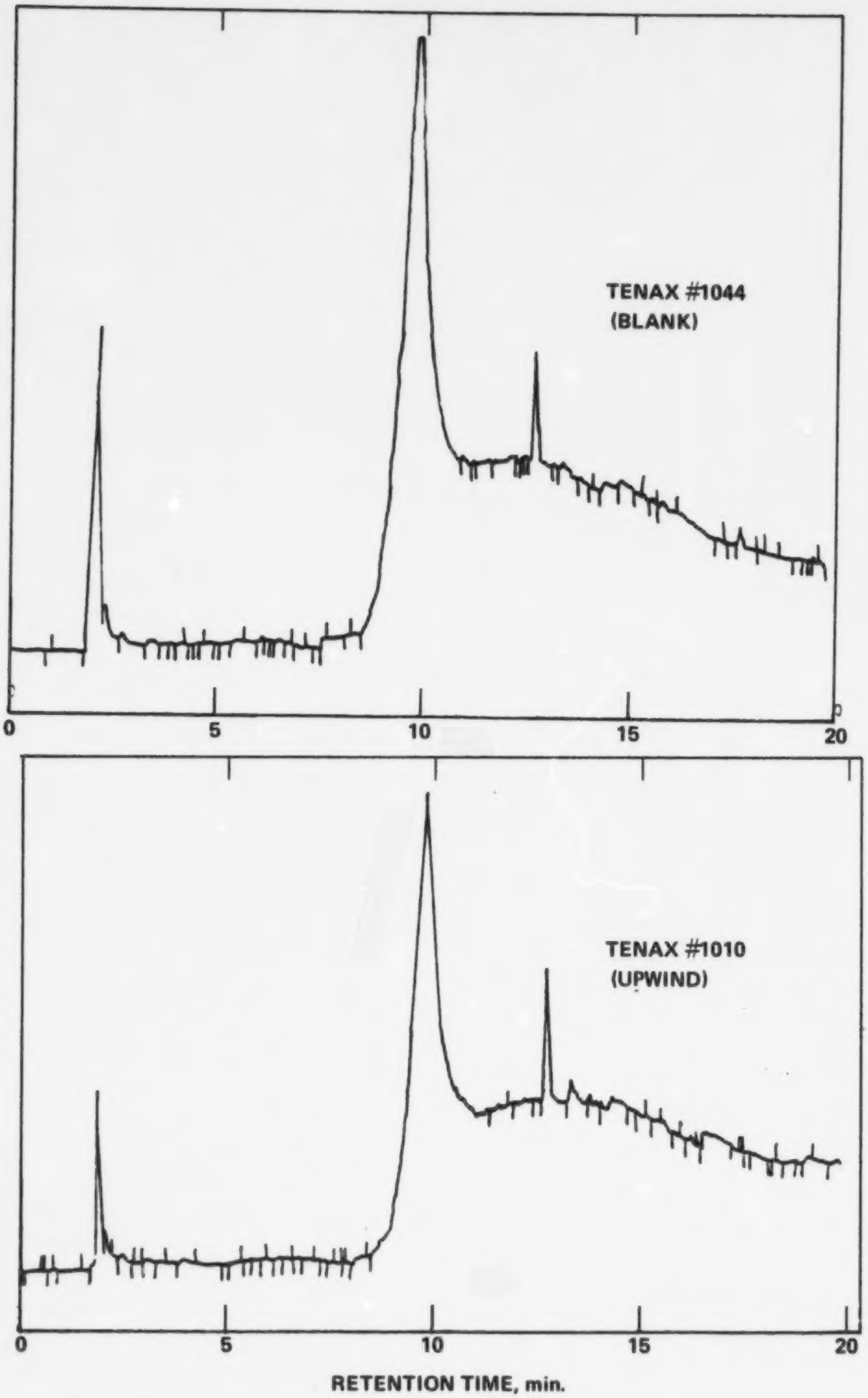

Figure 5. GC-HECD sulfur compound profiles for an upwind (#1010, day 6, site #1) and a blank (#1044) Tenax vapor trap extract (Reference 1).

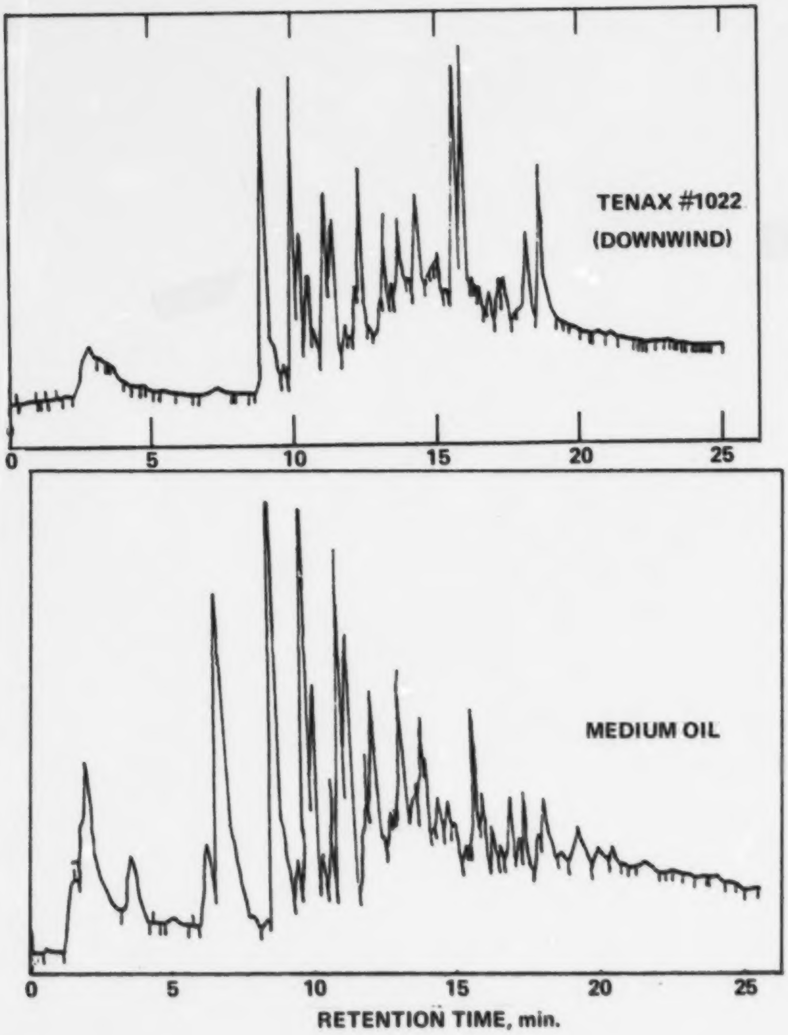

Figure 6. GC-HECD nitrogen compound profiles for a downwind Tenax vapor trap extract (#1022) and for Kosovo medium oil (Reference 1).

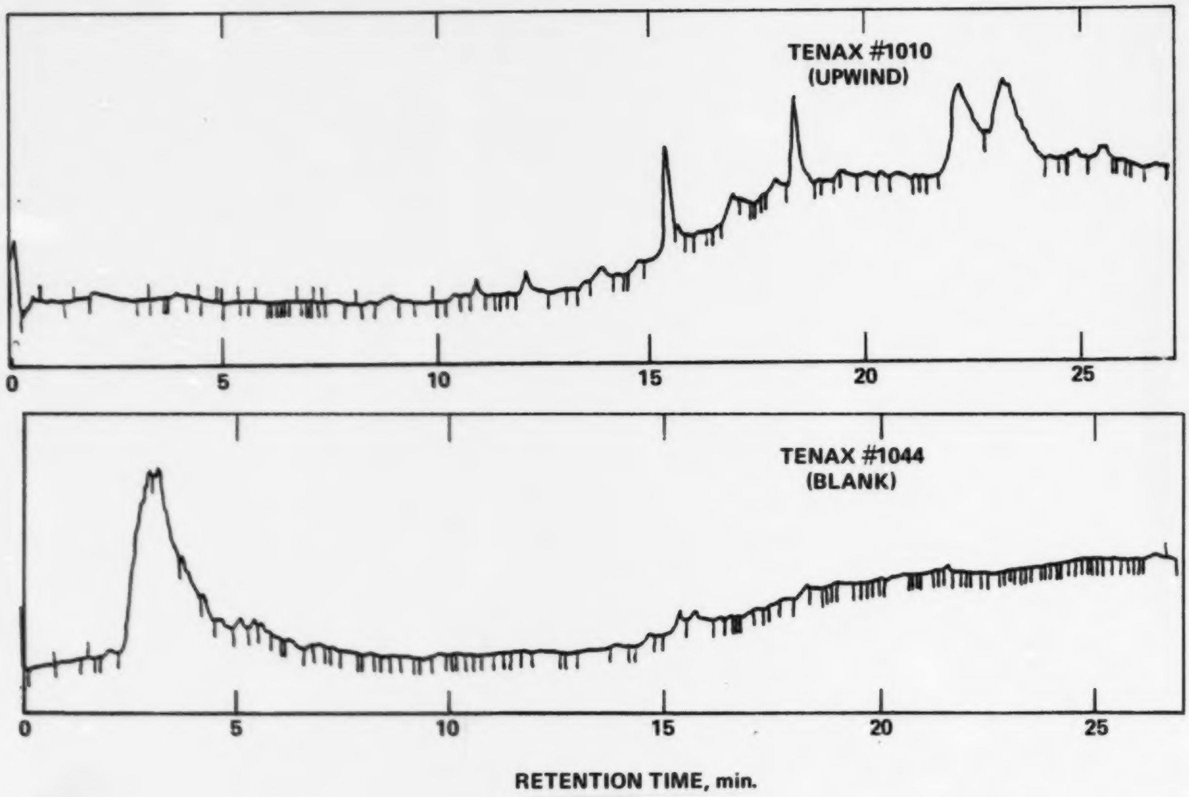

Figure 7. GC-HECD nitrogen compound profiles for an upwind (#1010) and a blank (#1044) Tenax vapor trap extract (Reference 1).

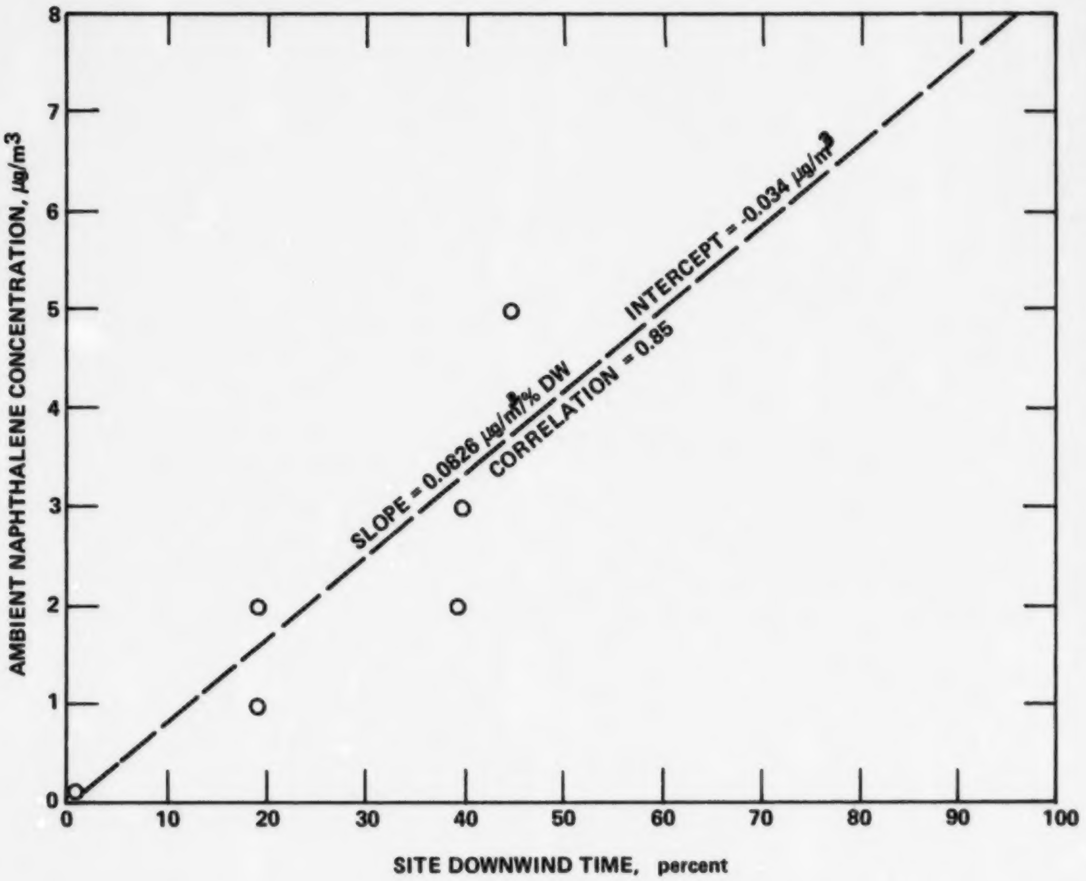

Figure 8. Correlation of organic loading in Kosovo ambient air with the percent of time the sampling site was downwind of the coal gasification plant (Reference 1).

indicates that certain species (e.g., benzopyrene isomer) may cause harmful health effects. A-MEG's are target value ambient air concentration levels below which the component is of low concern for its potential effects.

Griest, et al. (Oak Ridge National Laboratory)[17] used analytical procedures different from those of Radian and observed 120 vapor phase organics in the ambient air surrounding the Kosovo Industrial Complex. The 28 major components are listed in Table 2. The majority of the vapor phase organics were C_1-C_3 alkyl-substituted benzenes. Also present were diaromatics (such as naphthalenes and biphenyl) and several oxygenated species (such as benzaldehyde, acetophenone, phenol, and the cresols). Concentrations of individual constituents ranged from 0.02 to 9.0 $\mu g/m^3$, with toluene, phenol, benzaldehyde, and acetophenone being the major species in the vapor phase samples. Naphthalene, phenol, and the cresols were more concentrated in samples collected downwind of the gasifiers. Blanks were virtually featureless. (It should be noted here that the Tenax cartridges (200) used in this study were prepared by the Oak Ridge National Laboratory in October 1978.)

Approximately 100 aerosol phase constituents were observed in the gas chromatographic analysis of the unfractionated filter extracts. Filter blanks were featureless. As shown in Table 2, the major species were C_{19}-C_{36} n-paraffins and phthalates. In contrast to the vapor phase organics, the particulate phase organics appeared to be more aliphatic and approximately 2 to 3 orders of magnitude lower in concentration. N-paraffins ranged from 1 to 40 ng/m^3; the most concentrated particulate phase organic

Table 2. TENTATIVE IDENTIFICATION AND RANGE OF CONCENTRATIONS OF VAPOR AND PARTICULATE PHASE CONSTITUENTS IN SAMPLES COLLECTED NEAR YUGOSLAVIAN GASIFIER[e]

VAPOR PHASE		PARTICULATE PHASE	
TENTATIVE IDENTIFICATION	RANGE OF CONCENTRATION[a], $\mu g/m^3$	TENTATIVE IDENTIFICATION	RANGE OF CONCENTRATIONS, ng/m^3
BENZENE	0.33-1.8	BIPHENYL	0.29-4.2
n-C_9H_{20}	0.16-1.0	n-$C_{19}H_{40}$	1.8-11
TOLUENE	0.74-9.0	PHENANTHRENE	–[b]
n-$C_{10}H_{22}$	0.16-0.60	n-$C_{20}H_{42}$	0.44-2.0
ETHYL BENZENE	0.46-1.3	C_{14}-BENZENE	–[c]
m-XYLENE	0.20-1.3	n-$C_{21}H_{44}$	1.0-4.7
p-XYLENE	0.38-3.2	C_{14}-BENZENE	–[c]
o-XYLENE	0.24-1.6	n-$C_{22}H_{46}$	8.5-28
CUMENE	0.02-0.38	FLUORANTHENE (+ HYDROCARBON)	0.93-4.1
C_3-BENZENE	0.11-0.52	n-$C_{23}H_{48}$	5.4-13
C_3-BENZENE	0.25-2.0	n-$C_{24}H_{50}$	1.6-8.8
MESITYLENE	0.06-0.58	MW 256 + 274	–
C_3-BENZENE	ND-0.51	n-$C_{25}H_{52}$	6.2-18
C_3-BENZENE	0.21-2.2	n-$C_{26}H_{54}$	3.9-16
C_3-BENZENE	0.10-0.81	BIS-(2-ETHYL HEXYL)PHTHALATE	43-120
o-METHYL STYRENE	ND-0.11	MW 226[d]	–
BENZALDEHYDE	1.1-2.8	n-$C_{27}H_{56}$	19-40
ACETOPHENONE	1.3-3.0	n-$C_{28}H_{58}$	13-42
NAPHTHALENE	0.02-1.5	C_4-QUINOLINE	–[c]
2-METHYL NAPHTHALENE	0.03-0.25	n-$C_{29}H_{60}$	11-21
1-METHYL NAPHTHALENE	0.01-0.15	n-$C_{30}H_{62}$	2.2-7.9
PHENOL	0.16-2.3	BENZO(b,j, OR k)FLUORANTHENE	2.3-6.2
o-CRESOL	ND-1.0	n-$C_{31}H_{64}$	7.4-13
BIPHENYL	0.04-0.09	n-$C_{32}H_{66}$	1.4-7.2
INDOLE	0.02-0.13	n-$C_{33}H_{68}$	2.2-6.5
p-CRESOL	ND-0.24	n-$C_{34}H_{70}$	1.1-3.6
m-CRESOL	ND-0.36	n-$C_{35}H_{72}$	0.8-2.9
p-ETHYL PHENOL	ND-0.16		

[a] ND = NOT DETECTED.

[b] INCOMPLETE RESOLUTION PREVENTS QUANTITATION.

[c] STANDARD NOT AVAILABLE FOR QUANTITATION.

[d] NOT BENZO(ghi)FLUORANTHENE.

[e] FROM REFERENCE 17.

observed, bis-(2-ethyl hexyl) phthalate, ranged from 43 to 121 ng/m^3. Polycyclic aromatic hydrocarbons were approximately 10^{-1} as concentrated as the paraffins. Oak Ridge results were not weighted by percent downwind. Differences between upwind and downwind aerosol phase organics were not as apparent as those for the vapor phase organics. This result suggests that the vapor phase organics are a more sensitive indicator of the gasification plant's impact. However, further fractionation of the particulate phase organics may reveal more substantial differences than those observed from the profiles of the gross filter extracts.

CONCLUSIONS

Each of the Yugoslav ambient air study objectives was met. The adverse impact on the surrounding atmosphere of the Kosovo Industrial Complex, especially downwind, is unmistakable as described in the following conclusions:

- -Aerosols in the form of coal dust are a significant pollutant from the coal handling operation.
- -Aerosol emissions from the gasification process are overshadowed by aerosol emissions from coal handling.
- -Ambient aerosol levels exceed the primary and secondary U.S. National Ambient Air Quality Standards.
- -Aerosols appear to be carriers of PAH's.
- -The source of the PAH's in the aerosol collections is as yet unknown but may be the flare.
- -The level of benzo(a)pyrene exceeds the A-MEG's by a factor of 1000.

- Even though the light organic compounds were lost during sampling, benzene probably exceeds the A-MEG's by a factor of 10 to 100.
- Organic pollutants can be traced to the gasification plant.
- There is a broad range of organic compounds in the ambient air. The classes include aromatic and aliphatic hydrocarbons as well as their oxygen-, sulfur-, and nitrogen-containing derivatives.

Even though proposed U.S. facilities will be "better controlled" due to the use of state-of-the-art control technology and U.S. regulations, this study revealed areas of special concern on which emphasis should be placed when making decisions about the development, control, and placement of such facilities in the U.S. Such aspects as coal mining, processing, transport, and storage; process by-product storage and venting; fugitive emissions of organics throughout the process; and the storage of gasifier (and power plant) ash should be carefully reviewed. The Kosovo complex is a commercial scale facility, but only one tenth the size of proposed U.S. facilities. This study suggests that it is possible to differentiate between the emissions from a gasification plant and those from other sources near an industrial complex, and it also provides a unique data base for researchers as well as policy makers.

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Kombinat Kosovo, Pristina
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CHARACTERIZATION OF COAL GASIFICATION ASH LEACHATE USING THE RCRA EXTRACTION PROCEDURE

by

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ABSTRACT

Gasification ash constitutes the single largest solid waste stream from coal gasification facilities, and its disposal is subject to regulations promulgated under RCRA. Ashes from Lurgi gasifier, Wellman-Galusha gasifier and Texaco gasifier were subjected to the RCRA Extraction Procedure test. The results are reviewed in light of similar data on boiler ashes. Those findings indicate that these materials will not be considered toxic based on the 100X primary drinking water standard criteria.

1.0 INTRODUCTION

The Resource Conservation and Recovery Act of 1976 directs the Environmental Protection Agency to promulgate regulations to insure the proper disposal of solid wastes for the protection of both human health and the environment. With the recent reemphasis on America's coal resources, coal gasification may soon be providing a large amount of America's energy needs. As with all non-renewable energy resources, wastes will be generated in the production of the coal gas. Future commercial-scale gasifiers will need to be designed, constructed, and operated to protect human health and the environment. Solid wastes in the form of slags or ashes are produced from all coal gasification facilities. The proper disposal of these solid wastes will be a portion of this environmental protection.

To anticipate possible problems with solids disposal, the EPA has set forth a procedure to test the potential hazard of solid waste--the EP Toxicity Test.[1]

2.0 WASTE COLLECTION

Three coal gasifiers were sampled and the solid wastes subjected to the EP Toxicity Test. The data was compared to previous extraction tests performed on two ashes from a coal-fired boiler. To investigate the distribution of extractable metals among different sizes of ash, the Lurgi ash samples were divided into three size fractions; triplicates of each fraction were subjected to the EP test.

2.1 The Texaco Gasifier

Coarse slag was collected at the sieve screen used to separate the coarse slag from the slag water as the slag was blown down from the gasifier. A composited sample was taken over a 16-hour sampling period during gasification of a western subbituminous coal under conditions typical of a commercial operation.

2.2 The Wellman-Galusha Gasifier

Gasifier ash was sampled as the ash was transferred from the bottom of the gasifier to a storage bin. A dewatered composite sample was taken over a 12-hour sampling period. Cyclone dust samples were taken from the bottom of cyclone by raking the solid from the trough and allowing excess water to drain. Sampling was conducted during the gasification of a North Dakota lignite.

2.3 The Lurgi Gasifier

Unquenched Lurgi ash of three U.S. coals (Rosebud, Illinois #5 and Illinois #6) were furnished by the Peabody Company. The ashes were collected during a trial run at the Westfield gasification facility.

2.4 The Coal-Fired Steam Station

Precipitator ash was taken from the ash silo prior to removal by truck. Bottom ash was taken from the sluice pipe as it empties into the ash pond. A western lignite is normal boiler feed for the station.

3.0 RCRA TESTING PROCEDURE

The prescribed procedure is designed to roughly approximate the extracting of soluble material with rainwater. The solid is extracted with a sixteen-fold excess of leaching solution at a pH of 5.0 for a 24-hour time period at room temperature. Following the extraction period the sample is filtered and the final aqueous volume is made to 20 times the sample weight. The procedure followed is listed in Table 1. The extract is then analyzed for 8 metals which are listed in the EP and other constituents. Results are compared with the National Interium Primary Drinking Water Standards (NIPDWS) for eight metals:

- arsenic
- barium
- cadmium
- chromium
- lead
- mercury
- selenium
- silver

4.0 RESULTS AND DISCUSSION

Table 2 presents a comparison of the extract characteristics and the drinking water standards. Although the coal-fired boiler and the gasifiers operate at different conditions, the RCRA extract characteristics are in general quite similar. When compared to the 100X primary drinking water standards, none of the wastes analyzed are considered hazardous. This result is similar to those presented by other investigators working with different coal gasification ashes(3) and boiler ashes(4).

TABLE 1. RCRA EXTRACTION PROCEDURE(2)

- Weight 100g solid into extractor
- Add 1600 ml deionized water
- Measure the pH

  If less than 5.0, continue with extraction
  If greater than 5.0, add 0.5N ultrex acetic acid until pH 5.0. Check and readjust pH at intervals of 15, 30, 60, 120 minutes, if pH rises above 5.2.
- Extraction by shaking or stirring for 24 hours at 20°-40°C
- Filter through 0.45 micron filter
- Dilute to 2000 ml with deionized water

TABLE 2. CHARACTERISTICS OF WASTE EXTRACTS USING THE RCRA EXTRACTION PROCEDURE

	Concentration, µg/l													
	Ag	As	Ba*	Cd	Cr	Hg	Pb	Se	B*	Cu	Mn*	Ni	U*	Zn*
Lurgi-Rosebud														
3/8"-20 mesh	<0.2	<1	0.5	<0.1	<6	<0.4	<0.2	<1	0.55	2.7	3.22	34	<0.5	0.124
20-100 mesh	<0.2	2	1.0	1.1	<6	<0.4	1.0	<1	1.48	5.4	5.83	80	<0.5	0.157
<100 mesh	<0.2	3	2.3	2.0	<6	<0.4	1.8	<1	1.85	13.3	9.25	138	<0.5	0.321
Lurgi-Illinois #5														
3/8"-20 mesh	<0.2	<1	<0.2	52	5	<0.4	0.9	<1	0.28	5.6	0.39	4240	<0.5	37.1
20-100 mesh	<0.2	<1	0.8	32	3	<0.4	3.1	<1	0.77	6.5	1.15	442	<0.5	28.5
<100 mesh	1.6	3	1.0	26	4	<0.4	4.4	3	0.49	5.1	2.50	441	<0.5	9.2
Lurgi-Illinois #6														
3/8"-20 mesh	0.9	4	<0.2	13	3	<0.4	1.3	3	0.04	<2	0.28	49	<0.5	4.27
20-100 mesh	1.4	<1	<0.2	5.1	3	<0.4	1.3	<1	0.25	<2	0.39	56	<0.5	2.84
<100 mesh	<0.2	<1	<0.2	4.3	<2	<0.4	1.6	<1	0.20	<2	0.71	72	<0.5	1.13
Wellman-Galusha, ash	<1	19	1.0	<7	1	<0.6	7	14	--	--	--	--	--	--
Wellman-Galusha, dust	<1	33	1.0	<1	1	<0.3	8	6	--	--	--	--	--	--
Texaco, slag	<2	<2	0.19	37	4	<0.2	<2	<1	--	--	--	--	--	--
Boiler bottom ash	<1	<1	0.28	<0.3	<3	<0.2	<3	<1	--	--	--	--	--	--
Boiler fly ash	2	5	0.44	5.3	16	<0.2	<3	2	--	--	--	--	--	--
100x primary drinking water standard	5000	5000	100	1000	5000	200	5000	1000	--	--	--	--	--	--

*Values in mg/l

As expected, partly due to the larger surface area and partly due to the volatility of trace metals, the boiler fly ash contains slightly more extractable metals than the boiler bottom ash. For the Lurgi samples leachate metal concentrations were observed to be inversely proportional to the particle (ash) size for the Rosebud coal, but not necessarily for Illinois #5 or #6, suggesting surface phenomena could be one of the major factors controlling the leachability of metals in Lurgi gasifier ash.

As discussed before the Lurgi samples analyzed are unquenched ashes. Quenched ash is likely to contain even less extractable metals because a portion of the total extractable metals will be carried away by the quench water. However, all proposed commercial Lurgi plants plan to recycle process wastewater as quench water, and to achieve zero discharge (especially in the east where solar evaporation is not feasible) it has been proposed to evaporate the gas liquor in a forced evaporator, and to use the concentrated brine to moisten the ash. It is uncertain whether the practice would make the ash hazardous.

Table 3 presents the characteristics of Lurgi gas liquor, expressed in terms of μg/g of coal; also presented in Table 3 are the leachable metal contents of coal. As a worst case approach, one may assume all trace metals in the gas liquor ends up in the RCRA leachate, i.e.

Total leachable metal = extractable metal + soluble metal

Comparing the extractable metal (from ash) and the soluble metal (from gas liquor) data indicates that adding the soluble metal content will increase the extractable Se by 1½ times, the largest increase among all eight metals. Even so, the leachate concentration is calculated as seen in Table 4, to be 7 μg/l, still below the 100X primary drinking water standard. The RCRA leachate characteristics for Lurgi ash and boiler ash calculated based on this worst case scenario are presented in Table 4. Again, none of the metals exceeds the 100X drinking water standards.

Still, there are coals that contain much higher metal contents than the coals used in these studies. Table 5 presents the characteristics of the coals used in these studies and the maximum metal concentrations in coals

TABLE 3. EXTRACTABLE AND LIQUOR METAL CONCENTRATION IN COALS USED IN DIFFERENT GASIFIERS AND BOILER

Gasifier - Coal	Metal Concentration, μg/g								Ash Content
	Ag	As	Ba	Cd	Cr	Hg	Pb	Se	%
Extractable Metals Conc.*									
Lurgi - Rosebud	<0.52	7.7	5.9	5.2	<15	<1.0	4.6	<2.6	12.9
Illinois #5	4.1	7.7	2.6	130	13	<1.0	11	7.7	10.1
Illinois #6	3.6	10	<0.52	34	7.7	<1.0	4.1	7.7	9.2
Texaco - Western									
Subbituminous	<4.3	<4.3	0.41	80	8.6	<0.43	<4.3	<22	10.8
Wellman-Galusha									
(ash) No. Dakota Lignite	<1.4	26	1400	<9.5	1.4	<0.82	9.5	19	6.8
(dust) No. Dakota Lignite	<1.4	45	1400	<1.4	1.4	<0.41	11	8.2	6.8
Boiler (bottom ash) Western Lignite	<4.3	<4.3	1.2	<1.3	<13	<0.86	<13	<4.3	21.6
Boiler (fly ash) Western Lignite	8.6	22	1.9	23	69	<0.86	<13	8.6	21.6
Soluble Metal Conc.**									
Lurgi Liquor - Rosebud	0.041	0.41	<0.01	0.26	3.5	0.15	0.32	0.13	
Illinois #6	0.31	1.1	<0.2	<0.21	<0.21	1.25	6.3	10.5	
Total Leachable Metal Conc.***									
Lurgi (maximum)	4.4	11.1	<6.1	130	<19	<2.3	17	18	
Boiler bottom ash	<4.6	<5.4	<1.4	<1.6	<17	<2.1	<19	<15	
Boiler fly ash	8.9	23	<2.1	23	74	<2.1	<19	19	

*Extractable metal conc. = 20 x RCRA leachate conc. x % ash in coal

**Soluble metal conc = liquor conc. x $\frac{\text{liquor quantity}}{\text{coal feed}}$

***Total leachable metal conc. = extractable metal conc. + soluble metal conc.

TABLE 4. PREDICTED LEACHATE CHARACTERISTICS FOR LURGI ASH AND BOILER ASHES WHEN CO-DISPOSED WITH BRINE FROM CONCENTRATING LURGI GAS LIQUOR

	Leachate Characteristics,* μg/l		
Metals,	Lurgi Ash	Boiler Bottom Ash	Boiler Fly Ash
Ag	1.7	<1.1	2.1
As	4.3	<1.3	5.3
Ba**	<2.4	<0.32	<0.49
Cd	50	<0.37	5.3
Cr	<7.4	<3.9	17
Hg	<0.87	<0.49	<0.49
Pb	6.6	<4.4	<4.4
Se	7.0	<3.5	4.4

*Conc. = total extractable metal conc. ÷ (20 x % ash)
**Ba values in μg/ml; all other in μg/l

TABLE 5. METAL CONCENTRATIONS IN VARIOUS COALS AND RCRA LEACHATE CHARACTERISTICS BASED ON WORST CASE OIL

	Metals							
	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
Coal Characteristics, µg/g								
Rosebud(5)	0.06	1.2	87	0.4	4	0.11	0.51	0.33
Illinois #6(5)	--	1.0	--	<0.4	20	1.1	10	1.3
Western Subbituminous (Texaco)	0.3	<0.9	320	0.2	34	0.1	4	1.7
Lignite (Wellman-Galusha)	1	6.5	1300	0.4	10	0.39	2	1
Maximum Conc. in Coal(6)	0.08	120	1600	26	60	1.6	220	8.1
Predicted Max. Leachate Characteristics, µg/l								
Lurgi	2.2	470	43000	3300*	<88	52	240	78
Texaco	--	<270	950	4800*	7.1	<32	<110	<5
Wellman-Galusha, ash	--	<19	340	<20	<18	<0.82	<330	<8.1
dust	--	92	540	350	96	<0.82	<330	16

*Value exceeded the 100x drinking water standards found in open literature.(6) The leachability characteristics of other coals is not known, but as a first approximation one may assume the leachable metal content is proportional to the total metal content. The predicted maximum leachate characteristics thus derived are presented in Table 5. As the predictions indicate, only cadmium in both the Lurgi ash and Texaco slag exceed the 100X drinking water limit. It should be emphasized that the above assumption is very conservative as, undoubtedly, other factors such as mineralogy will play a major role in controlling the leachable metals. Furthermore, it is uncommon to encounter coals with as high a Cd concentration (26 ppm). Of the samples analyzed by Gluskoter, et al,(6) only about 6% had Cd values in that range, with over 90% having less than 1 ppm Cd.

Additional data on the leachate characteristics of other coals/gasifiers are expected to be available by next year. As an ongoing EPA program, Radian is presently testing the ash collected from a Lurgi facility in Kosovo, Yugoslavia, and TRW is scheduled to sample a Koppers-Totzek facility in Modderfontein, South Africa, early next year.

5.0 CONCLUSION

The RCRA EP Toxicity Test as performed on the ashes from a Lurgi gasifier, a Texaco gasifier and a Wellman-Galusha gasifier indicates these materials will not be considered hazardous wastes based on the toxicity criterion alone. Based on the metal contents in the ash and in the Lurgi gas liquor, co-disposal of the gas liquor with the gasifier ash also will not be considered hazardous. However, Lurgi gas liquors are known to contain aromatic organics, some of which are priority pollutants. Unless these organics are removed prior to co-disposal with ash, EPA may eventually list this as a hazardous waste.

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COMPARISON OF COAL CONVERSION WASTEWATERS

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This paper presents the analytical results obtained from the aqueous process condensates from an oxygen-blown, lignite-fired Lurgi gasifier, an air-blown, bituminous-fired Chapman gasifier and a coke oven process. Results show that strong similarities exist between the two gasifier process condensates. These similarities include both gross chemical parameters and the concentrations of specific organic compounds. Extraction of the three condensates using diisopropyl ether resulted in a 99+ percent removal of total phenols and a 75 percent average removal of the total organic carbon (TOC). Further extraction with an exhaustive technique only removed an average of 9 percent of the remaining TOC from the two gasifier waters. The <500 MW to >500 MW ratio was approximately two for the remaining refractory organics. The results of a brief study using activated carbon to remove the refractory organics indicated that the TOC levels could be further reduced, but the levels remained relatively high. The occurrences of eight nitrogen-containing organic species were compared using a gas chromatograph equipped with a Hall Electrolytic Conductivity Detector in the nitrogen-specific mode. The occurrences of phenolic species were also compared using a gas chromatograph equipped with a flame ionization detector. The three process condensates contained the same phenolic and nitrogen heterocyclic compounds.

COMPARISON OF COAL CONVERSION WASTEWATERS

INTRODUCTION

Three coal conversion process condensates were characterized as part of Radian Corporation's overall effort to perform a comprehensive environmental assessment of low- and medium-Btu coal gasification technology for the U.S. Environmental Protection Agency. The overall program is being directed by the Fuel Process Branch of EPA's Industrial Environmental Research Laboratory in Research Triangle Park, North Carolina.

The objective of this study was to compare the composition of the condensates and to screen for possible steps in treatability. The three aqueous condensates and the reasons they were chosen are as follows:

Wastewater	Rationale
Lurgi (Process Condensate)	Proposed for commercial plants in the United States
Chapman (Recycled Process Condensate)	Currently available in the United States and possible similarities in composition to Lurgi
Coke Oven (Process Condensate Spray Down)	Extensive data available on treatability and possible similarities in composition to Lurgi

PROCESS DESCRIPTIONS

The three processes will be described briefly in this section. Where the samples orginated in the processes will be shown.

In Figure 1, a schematic diagram of the Lurgi Gasification Process is illustrated. The main points to notice are the quench and cooling towers which condense water along with the organic and inorganic components from the product gas, and the separator where the aqueous layer is separated from the

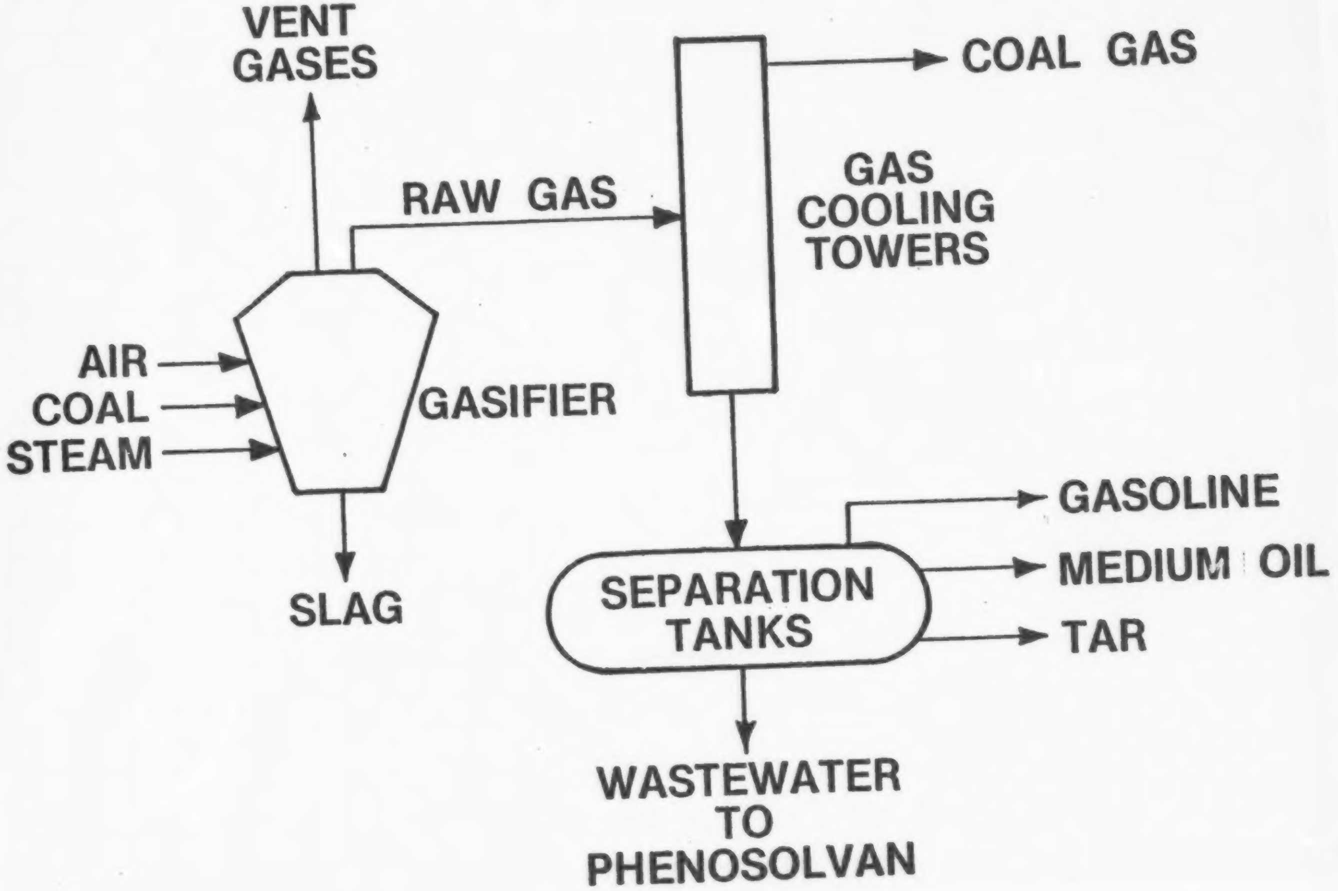

VENT GASES
AIR
COAL
STEAM
GASIFIER
SLAG
RAW GAS
GAS COOLING TOWERS
COAL GAS
SEPARATION TANKS
GASOLINE
MEDIUM OIL
TAR
WASTEWATER TO PHENOSOLVAN

Figure 1. Schematic diagram of the Lurgi Gasification Process.

tars and oils. The Lurgi condensate was obtained from the exit point of the aqueous layer from the separator. The plant sampled for this study was an oxygen-blown, lignite-fired Lurgi gasification plant in the Kosovo Region of Yugoslavia.

The Chapman-Wilputte Gasification Process is illustrated in Figure 2. The aqueous layer after separation of the tars and oils is recirculated to the gas quenching/cooling processes. A grab sample of the wastewater was obtained from the aqueous layer in the separation tank. The plant sampled was located near Kingsport, Tennessee and was equipped with an air-blown, bituminous-fired Chapman gasifier.

The coke oven system is illustrated in Figure 3. Even though coking may at first appear to be very different from a gasification process, there are many similarities. The design is different from either a Lurgi or Chapman facility but, again, as illustrated, there is a gas quenching and cooling system to cool the gases and remove water, tars, and oils. The quench liquor is sent to a separator where tars/oils are separated from the aqueous layer. Part of the water layer is recirculated and the rest is treated. The condensate sample was obtained at the point where the excess aqueous layer exits the separator.

RESULTS AND DISCUSSION

The following subsections will detail the results of the different types of analyses and will contain brief discussions on treatability. These sections will include:

- water quality parameters,
- extractions of organics,
- concentrations of phenols,

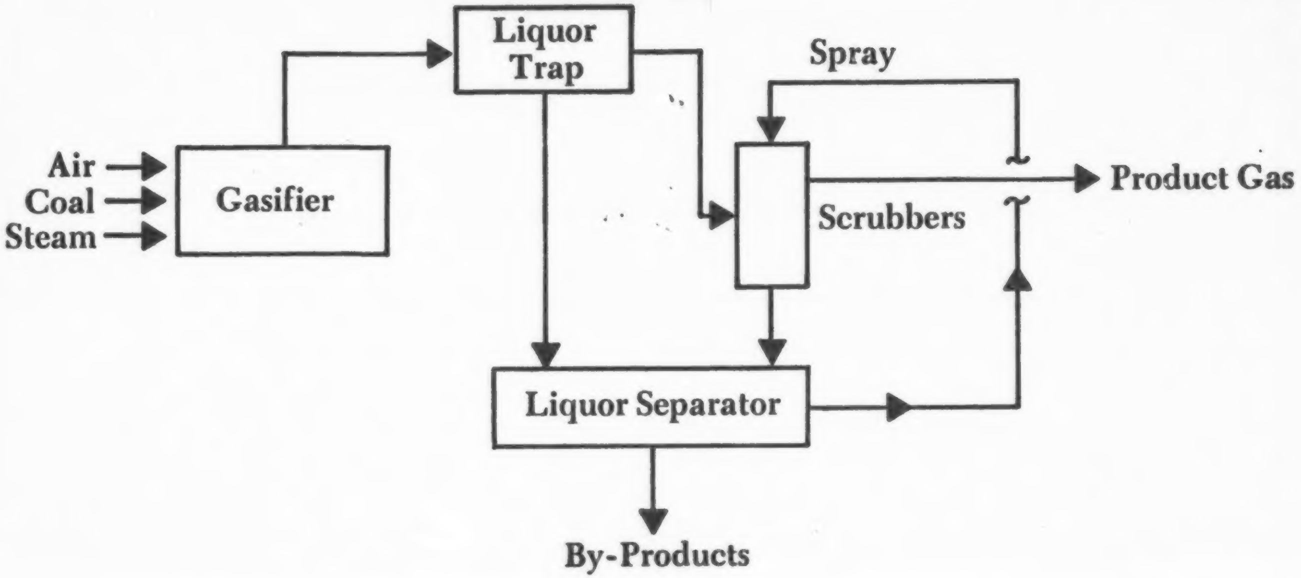

Air
Coal
Steam
Gasifier
Liquor Trap
Spray
Scrubbers
Product Gas
Liquor Separator
By-Products

Figure 2. Flow diagram of Chapman facility.

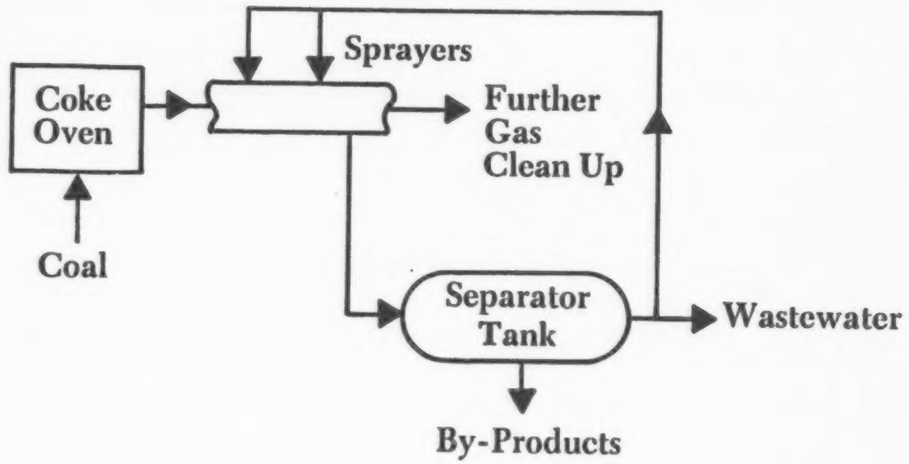

Sprayers
Coke Oven
Further Gas Clean Up
Coal
Separator Tank
Wastewater
By-Products

Figure 3. Flow diagram of coke oven.

- concentrations of nitrogen-containing organics,
- molecular weight distribution of refractory compounds, and
- removal of refractories.

Water Quality Parameters

The water quality parameters for all three process condensates are listed in Table 1. In general, the parameters are very similar for the condensates from the two gasification processes using two different coals (lignite and bituminous). The water quality parameters for the coke oven process condensate are generally lower than the other two process condensates.

Biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) are specific measurements where the process condensates of the Lurgi and Chapman gasification processes are similar. The differences among the three condensates may be caused by the types of coal being used. For instance, the lignite from the Kosovo region of Yugoslavia used in the Lurgi Process may contain much less phosphorous than the coal for the Chapman Process. Of course, differences in the process conditions may also affect the composition of the aqueous condensate. Differences may also be caused by Chapman recirculating the water, whereas the Lurgi does not recirculate it. Therefore, higher levels would be expected in the Chapman aqueous condensate. To test the process effects would require using the same coal at both facilities.

Extractions of Organics

Two extraction procedures were used on the three aqueous condensates. The first extraction procedure was designed to mimic the Phenosolvan Process used by Lurgi to remove phenols from process wastewaters. Three volumes of diisopropyl ether (each equal to 1/3 the sample volume) were added, one at a time, to the aqueous condensate. The samples were then shaken vigorously

Table 1. WATER QUALITY PARAMETERS FOR THREE COAL CONVERSION AQUEOUS PROCESS CONDENSATES

Water Quality Parameters (mg/ℓ)	Aqueous Process Condensates		
	Lurgi	Chapman	Coke Oven
BOD	12,200	15,900	3,420
COD	20,200	28,500±1,100	4,860±390
TOC	6,490	9,430	6,160
NH_3-Nitrogen	4,340	8,130±90	2,850±0
Total Kjeldahl Nitrogen	4,010	9,420	3,160
Nitrate-Nitrogen	<0.5	<0.5	<0.5
Total Phosphate-Phosphorous	0.12	5.48	0.21
Total Acid Hydrolyzable Phosphate-Phosphorous	0.08	5.48	0.21
Phenol	3,030	2,130±110	1,140
Oil and Grease	917	540	700
Cyanide	<0.02	59±1	69±1
Thiocyanate	83	1,450	570
Sulfide	<10	207±12	241±18
TDS	2,010	48,600	4,870
TVDS	1,890	42,300	4,700
TSS	417	11	20
TVSS	402	11	18

for two minutes and allowed to stand in a separatory funnel until the layers separated. Then the ether layer was removed.

The second extraction procedure followed the above steps except that methylene chloride and diethyl ether substituted for the diisopropyl ether and the aqueous layer was extracted at both pH equal to <2 and >12. This procedure will be labeled the "analytical extraction" procedure. This procedure was used to show if changes in pH and solvent would increase the amount of organics removed from the aqueous layer.

In Table 2, the effects of the two sequential extractions on selected water quality parameters are listed. The diisopropyl ether (DIPE) extraction eliminated greater than 99+ percent of the phenol (phenolic content) from all three process condensates. The oil and grease measurements also dropped below the detection level of 10 mg/ℓ for all the condensates. The BOD, COD, and TOC values were reduced significantly by the DIPE extraction.. The exhaustive, analytical extraction did not significantly reduce the values of the water quality parameters when applied to the waters after DIPE extraction.

The organic carbon left in the aqueous phase after the two extractions was classified as refractory organic compounds. These refractories are important because Phenosolvan treatment alone leaves them in the aqueous phase and they must be addressed in further treatment steps. The relative amounts of refractories (non-extractables) as measured by TOC are graphically illustrated in Figure 4. The refractories must be very polar and/or ionic in nature since both the extraction procedures (including pH adjustment) would not remove them.

For further characterization of the refractories, the molecular weight distribution above and below 500 was determined by gel permeation chromatography. This separation, as measured by TOC, is illustrated in Figure 5 for the aqueous condensates of the gasification processes. The relative

Table 2. EFFECTS OF THE DIPE EXTRACTION AND THE ANALYTICAL EXTRACTION (SEQUENTIAL) ON SELECTED WATER QUALITY PARAMETERS IN THE THREE AQUEOUS PROCESS CONDENSATES

Water Quality Parameters	Process Condensate								
	Lurgi (mg/ℓ)			Chapman (mg/ℓ)			Coke Oven (mg/ℓ)		
	Raw	DIPE	Analytical	Raw	DIPE	Analytical	Raw	DIPE	Analytical
BOD	12,200	3,080	ND*	15,900	2,800	ND	3,420	727	ND
COD	20,200	4,940	4,270	28,500±1,100	15,500	7,230	4,860±390	2,770	1,690
TOC	6,490	2,010	1,894	9,430	3,290	1,830	6,160	602	477
Phenol	3,030	8.9	ND	2,130±10	3.0	ND	1,140	9.4	ND
Oil & Gas	917	<10	ND	540	<10	ND	700	<10	10

*Not Determined

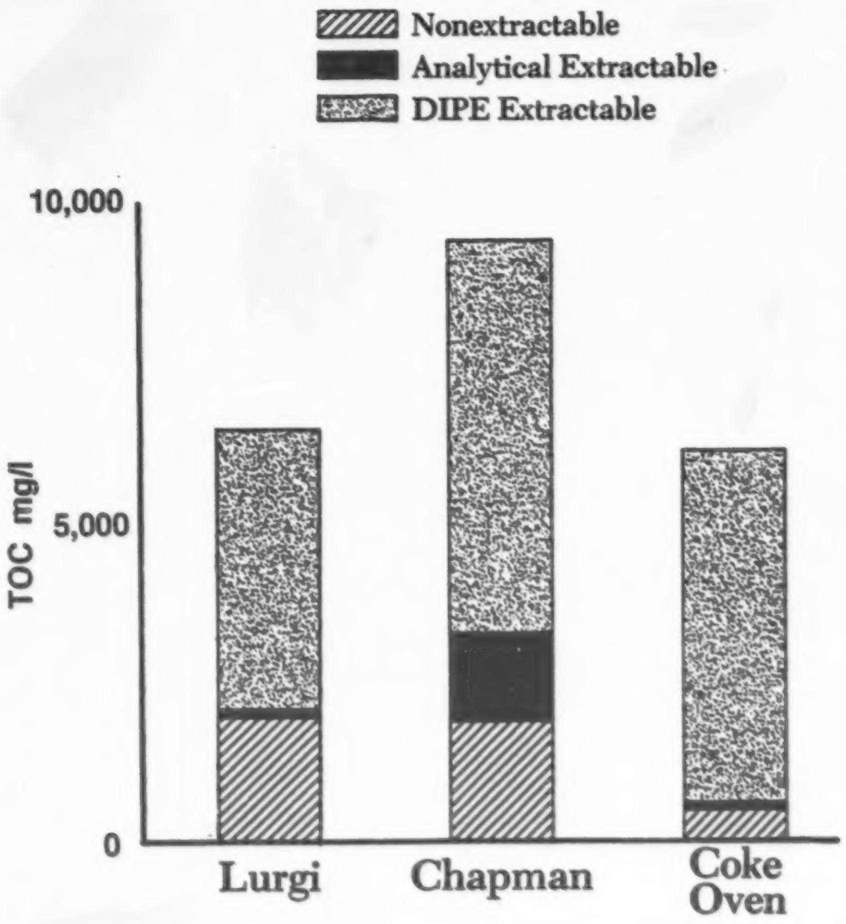


Figure 4. Amounts of total organic carbon removed by the DIPE and Analytical Extraction Techniques.

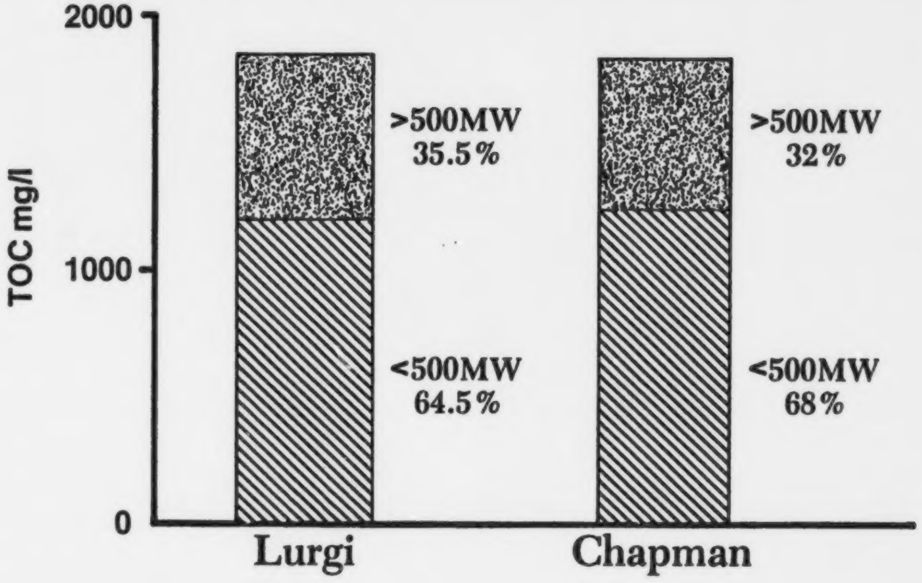


Figure 5. Molecular weight distribution of refractory organics.

amounts of the refractories and their molecular weight distribution are the same within experimental error for the Lurgi and Chapman waters. This strongly suggests that the Chapman aqueous condensate, after DIPE extraction to mimic phenol removed by Phenosolvan, can be used as a model for treatment studies of Lurgi-produced wastewater.

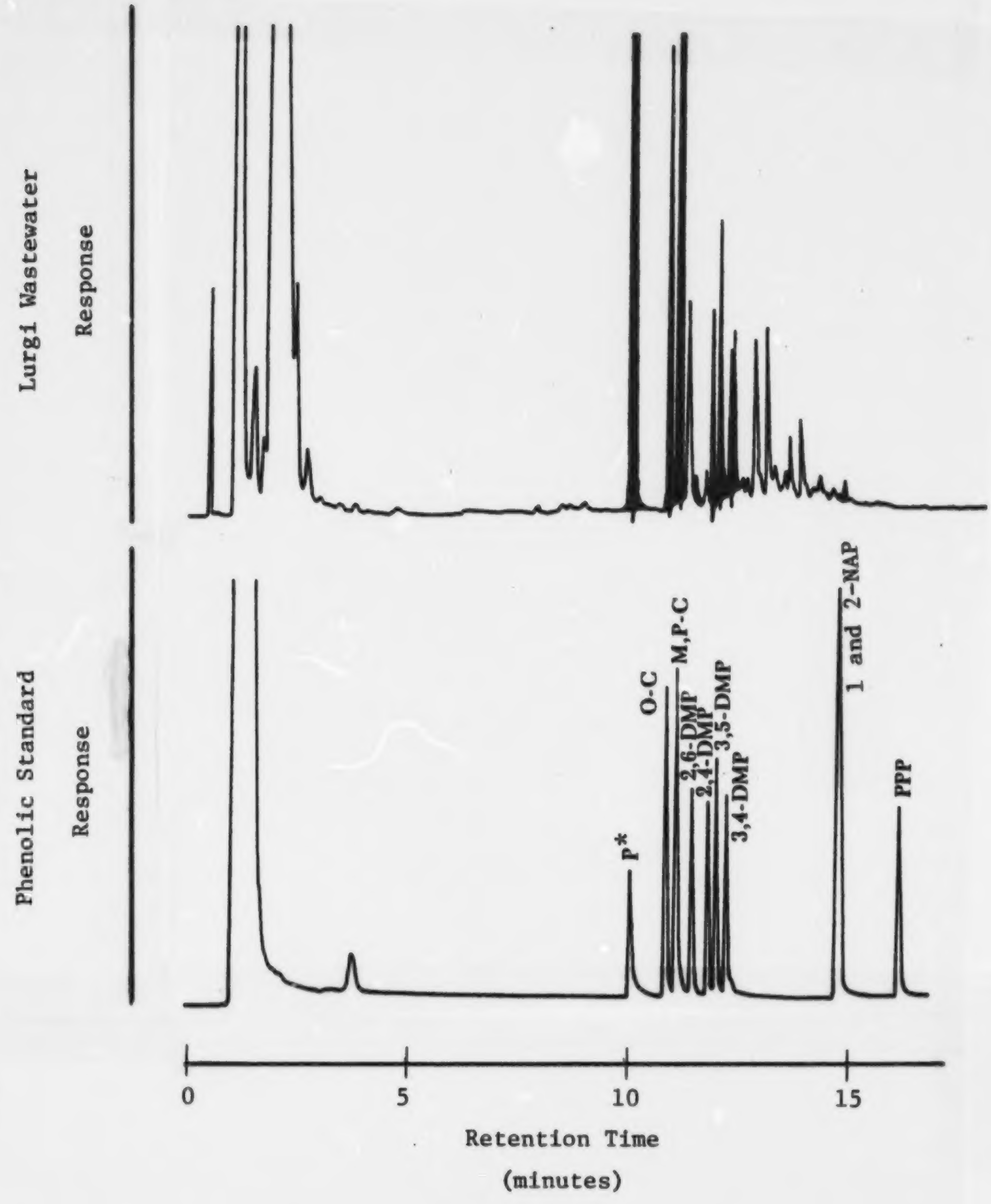
Concentrations of Phenols and Nitrogen-Containing Compounds

Another indication that the aqueous process condensates are similar is the distribution of phenolic and nitrogen-containing compounds. Most of these compounds were removed by the DIPE extraction; therefore, an analysis of the DIPE layer was performed.

Figure 6 compares a standard consisting of 11 phenolic compounds to the organics extracted by DIPE from the LURGI wastewater. These chromatograms were produced by a gas chromatograph equipped with a flame ionization detector. The shaded peaks in the DIPE extract match the retention times of the phenolic standards. This suggests that the major portion of organics in the Lurgi wastewater is phenols. Similar results were observed for the Chapman and coke oven process condensates.

Table 3 contains a list of the concentrations of the phenolic compounds found in the three process condensates. The phenolic species show a very strong correlation even in concentrations between the two gasification processes. Again, as in the water quality parameters, the coke oven phenolics were found at lower concentrations than those in the gasification condensates. The same species, however, were present in all three aqueous process condensates.

Trace species in the form of nitrogen-containing compounds were analyzed in the DIPE extracts of all three process condensates. The results of the semiquantitative analysis are listed in Table 4. Even at trace levels, all three aqueous process condensates contained the same nitrogen heterocyclic compounds. Even though the data is semiquantitative, the relative



***See Table 3 for the names of the phenols.**

Figure 6. Chromatograms of DIPE extractable organics from Lurgi wastewater and an eleven compound standard of phenols.

Table 3. PHENOL SPECIATION DATA FOR THE DIPE EXTRACTS OF THE THREE AQUEOUS PROCESS CONDENSATES

Compound	Aqueous Process Condensate Lurgi (mg/ℓ)	Chapman (mg/ℓ)	Coke Oven (mg/ℓ)
Phenol	1,740±100	1,460±170	888±52
o-Cresol	406±27	420±54	70.0±2.3
m&p-Cresol	1,040±60	1,120±120	279±14
2,6-Dimethylphenol	33.1±10.0	19.1±0.2	2.2±1.0
2,4-Dimethylphenol	172±17	196±27	14.5±0.1
3,5-Dimethylphenol	266±21	172±24	23.4±0.8
3,4-Dimethylphenol	271±24	681±82	41.5±1.3
1&2-Naphthol	13.0±30.6	14.5±0.3	4.5
p-Phenylphenol	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$

Table 4. NITROGEN-CONTAINING ORGANIC COMPOUNDS IN THE DIPE EXTRACTS OF THE THREE AQUEOUS PROCESS CONDENSATES (SEMIQUANTITATIVE DATA)

	Aqueous Process Condensate		
Compounds*	Lurgi (mg/ℓ)	Chapman (mg/ℓ)	Coke Oven (mg/ℓ)
Pyridine	12	2	11
2-Methylpyridine	19	5	11
3-Methylpyridine	45	11	12
Ethyl/Dimethylpyridines	7	1	1
Trimethyl/Ethylmethylpyridines	27	17	28
C_4-pyridines	18	17	14
Quinoline	9	10	30

*All compounds quantified as pyridine.

concentrations of the compounds within each of the condensate extracts are virtually identical as listed in Table 4.

Removal of Refractory Compounds by Activated Carbon

The graph in Figure 7 illustrates the removal of the refractory compounds with activated carbon. TOC measurements indicated the amounts of organics remaining in the water after the addition of varying amounts of activated carbon. The initial amount of activated carbon (0.005 g/mℓ) removed most of the organic matter that could be removed. Additional amounts of activated carbon, up to a ratio of 0.1 g activated carbon per milliliter of wastewater, did not significantly increase the amount of refractory compounds removed. The activated carbon was effective in taking out the color species in the wastewater.

CONCLUSIONS

The following statements summarize the conclusions of this brief study.

- Water quality parameters are similar in the three aqueous process condensates with coke oven condensates having lower values.
- The same phenolic compounds were found in each process condensate. Levels of these compounds were similar in the gasification condensates. The coke oven condensate had lower levels of phenols.
- The same trace nitrogen species were found in all three condensates.
- Levels of nonextractable organics were similar in the Chapman and Lurgi condensates.

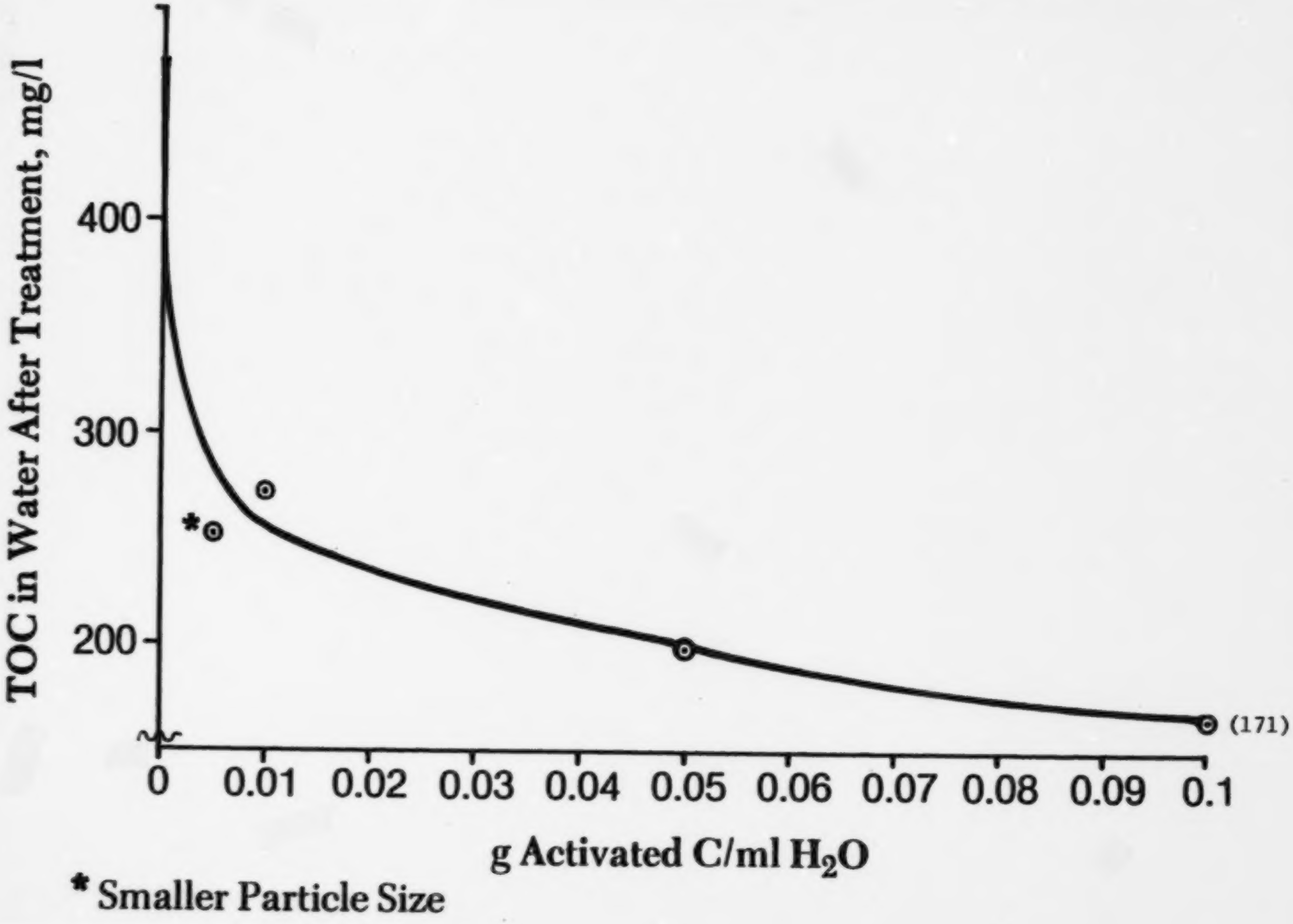


Figure 7. Removal of organics from the extracted Lurgi wastewater by activated carbon.

- Treatability of gasification wastewaters:
    - may not be similar to coke oven treatment because of nonextractables;
    - may not be sufficiently polished by activated carbon due to high residual TOC levels; and
    - can be studied using the Chapman process condensate as a good model for the Lurgi wastewater.

Session IV: ENVIRONMENTAL CONTROL

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RANKING OF POTENTIAL POLLUTANTS FROM COAL GASIFICATION PROCESSES

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ABSTRACT

Potential pollutants associated with coal gasification processes were studied based on data from the EPA environmental assessment research program. An environmental assessment methodology based on health and ecological Multimedia Environmental Goals (MEGs) is described and applied to product, byproduct, process and waste streams. A list of chemical species that were measured or qualitatively identified in coal gasification streams is given. Maximum concentrations of each quantitated species in each medium (solid, liquid, gas, tar) are given. Production factors have been computed and normalized on the basis of coal input rate to facilitate comparisons. Chemical species have been ranked by potential hazard to health and ecology. Priorities for monitoring, regulation and control technology development may be established from these lists.

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RANKING OF POTENTIAL POLLUTANTS FROM COAL GASIFICATION PROCESSES

INTRODUCTION

This study was initiated to compile the various source and laboratory (experimental) test results on potentially hazardous species which have been obtained under the EPA synthetic fuels environmental assessment program. The compilation has been developed in the form of listed chemical constituents which are ranked on the basis of their potential hazard. Since the data represent various gasifiers, coal types, operating conditions and configurations, and since the effluents are variable in their physical and chemical nature and their quantity, a systematic approach was needed to place the results on a common basis for comparison and/or ranking.

The information and results are needed to help provide direction to future environmental assessment activities, to focus EPA and interagency health/ecological effects testing on compounds and mixtures of greatest concern, and to assist EPA program and regional offices in the establishment of appropriate regulations, criteria, guidelines and permit policies.

The achievement and maintenance of an acceptable (or quality) environment must from a practical viewpoint involve the establishment of maximum allowable concentrations of chemical contaminants in the air, water, and land which constitute the natural environment. Such concentrations may be referred to as Multimedia Environmental Goals (MEG) values. Discharge MEGs (DMEGs) represent approximate concentrations for contaminants in source emissions to air, water or land which will not evoke significant harmful or irreversible responses in exposed humans or ecology when these exposures are limited to short duration. DMEGs for human health and ecology have been developed for use in assessing the impact of effluent discharges.[1-4]

A number of coal gasification operations are currently active around the world. Direct coal and (oil shale) liquefaction may be proved to be technically feasible and economically acceptable in the future; these alternatives may require special processing of the potential product to meet acceptable market specifications, and significant costs may be incurred to accommodate process residuals.

In this study, the chemical analyses of coal gasification product, byproduct, discharge and process streams sampled and analyzed by the Radian Corporation during four source testing programs have been subjected to an environmental assessment analysis based upon multimedia environmental goals. A similar analysis of data obtained from the laboratory coal gasification system at Research Triangle Institute (RTI) has also been conducted.

Radian Corporation Source Tests

The Radian Corporation has conducted source tests at four operating coal gasification facilities. Two Wellman-Galusha units located at York, PA and Ft. Snelling, MN were sampled as well as a Lurgi gasifier in Kosovo, Yugoslavia and a Chapman (Wilputte) gasifier located at Kingsport, TN. A variety of products, byproducts, process streams and effluents were sampled at the different sites. The sampling strategies did not yield data that were directly comparable. Sampling was not meant to be exhaustive but was designed to focus on streams of potential environmental significance.

The Wellman-Galusha gasifier at York, PA converts anthracite coal into fuel gas used for brick manufacturing at the Glen Gery Brick Company.[5] Data on five different streams were available for this study: two solid wastes, the gasifier ash and cyclone dust, one liquid stream, the ash sluice water and two gaseous streams, the poke hole gas and coal hopper gas.

The Wellman-Galusha gasifier at Ft. Snelling, MN uses North Dakota Indian Head lignite as a feedstock for low Btu gas production. Data on seven different streams were available for this study: two solid streams, the gasifier ash and cyclone dust, three liquid streams, the cyclone quench water, ash sluice water, and service water and two gas streams, the product gas and the coal bin vent gas. As no flow rate was available for the coal bin vent gas, a limited environmental assessment approach to gaseous effluents was taken.

The Chapman (Wilputte) gasifier at Kingsport, TN converts low sulfur Virginia bituminous coal to low Btu guel gas.[6] Data on four effluent streams were available. Three solid streams--the cyclone dust, gasifier ash, and byproduct tar, two gaseous streams--the coal feeder vent gas and separator vent gas and the separator liquor, a recycled aqueous stream were sampled.

Data on 18 gaseous streams and three liquid streams sampled at the Lurgi gasifier at Kosovo, Yugoslavia,[7-9] were used in this study. This plant converts Yugoslavian lignite to medium Btu fuel gas. Of the gaseous streams, eight were discharges and 10 were process streams. The gaseous discharges were the autoclave vent gas, coal bunker vent gas, CO_2-rich Rectisol gas, tar tank vent gas, medium oil tank vent gas, phenolic water tank vent gas, degassing column gas and gasoline tank vent gas. The cyanic water and the inlet and outlet from the Phenolsolvan unit are aqueous process streams that were sampled. No solid stream data were available.

RTI Gasifier Tests[10-12]

Data from 10 selected semicontinuous, fixed-bed tests of the RTI laboratory gasifier were analyzed in detail. In each case the solid gasifier ash and the aqueous condensate stream were the two discharges sampled. Two additional streams, the product gas and the byproduct tar (considered a solid) were also sampled. The 10 selected tests involved steam/air gasification of North Dakota Beulah/Zap lignite, Montana Rosebud/ McKay and Wyoming Smith/Roland subbituminous coals, Illinois No.6 and Western Kentucky No.9 bituminous coals and Pennsylvania Bottom Red Ash anthracite.

ASSESSMENT METHODOLOGY

Multimedia Environmental Goals (MEGs) form the basis for the environmental assessment methodology developed under the guidance of the Fuel Process Branch of EPA/IERL/RTP. Each component or species is assigned discharge multimedia environmental goal (DMEG) and ambient multimedia environmental goal (AMEG) values.[1-4] Individual DMEG values for a substance are related to the health or ecological effects of that substance; DMEG is the estimated concentration of the substance which would cause minimal adverse effects to a healthy receptor (man, animal, plant) which is exposed only once, or intermittently for short time periods. (AMEG values are similar except that they are based upon a continuous, rather than single or intermittent, exposure period.

DMEG values generally carry two subscripts, be they explicit or implicit. The first defines whether the value refers to air (a), water (w), or land (l); the second, whether the value refers to human health (h) or the ecological environment (e). In this study the health-based DMEG values were used primarily. The ecology-based DMEG values were used only to generate a comparative ranking of pollutants. No AMEGs were used in this study.

Discharge severity (DS) is a measure (index) of the degree to which the concentration of a particular substance is at a potentially hazardous level in a discharge (effluent.)[13] DS is dimensionless. It is computed as the concentration of the substance in a discharge divided by the DMEG value for that substance. DS may thus carry two subscripts, in general; one represents the phase and the other whether the potential harmful effects are health or ecological in nature.

Production factors based on coal input rates have been developed from the chemical analytical data available. These production factors have the dimensions of mass/mass; specifically, the units μg produced/g coal input have been used. Production in all measured product, byproduct and discharge streams is included in these figures and maxima among all sources considered in the study were selected.

ASSESSMENT RESULTS

The complex heterogeneous nature of coal gives rise to a wide variety of organic compounds in the streams resulting from coal conversion processes. Table 1 lists the organic compounds identified during the four Radian Corporation source tests as well as those identified from operation of the RTI laboratory gasifier over the last four years. Within each MEG category, the compounds that have been quantitated are given first, followed by those that have been identified but not measured. In addition, a large number of inorganic compounds and elements have also been identified.

The maximum concentrations measured in the various media are presented in Tables 2 through 4. Because of their particular properties, tars have been considered to be a separate medium in these tables. The concentration

TABLE 1. ORGANIC COMPOUNDS IDENTIFIED IN COAL GASIFICATION STREAMS

MEG Category	Name
1. Aliphatic Hydrocarbons	methane
	ethane
	propane
	butanes
	isobutane
	alkanes $>C_6$
	methylcyclohexane
	alkanes $\geq C_{13}$
	C_3-hydrocarbons
	C_4-hydrocarbons
	C_5-hydrocarbons
	C_{6+} hydrocarbons
	ethylene
	propylene
	acetylene
	phenylacetylene
	n-pentane
	isopentane
	n-hexane
	2-methylpentane
	3-methylpentane
	n-heptane
	n-octane
	n-nonane
	n-decane
	n-undecane
	n-dodecane
	n-tridecane
	n-tetradecane
	n-pentadecane
	n-hexadecane
	methylcyclobutane
	cyclopentane
	cyclohexane
	dimethylcyclohexane
	trimethylcyclohexane
	cyclooctane
	dimethyldecahydronaphthalene
	butene
	isobutene
	hexene
	1-pentene
	2-methyl-1-butene
	1,3-butadiene
	pentadiene
	cyclopentene
	cyclohexene
	cyclopentadiene
	ethyne
	propyne
2. Alkyl Halides	dichloromethane (artifact)
	trichloromethane (artifact)
	carbon tetrachloride (artifact)
3. Ethers	anisoles
	methylanisole
	diethylether
	phenyl-2-propynylether
	1-methoxynaphthalene
	2-methoxynaphthalene
	3,6-dimethoxyphenanthrene
	2-methoxyfluorene
5. Alcohols	aliphatic alcohols $>C_6$
	aliphatic alcohols $\geq C_{13}$
	alkylalcohols $>C_6$
	alkylalcohols $>C_{13}$
	3,5,5-trimethyl-1-hexanol
7. Aldehydes, Ketones	acetophenone
	acetaldehyde
	butanal
	pentanal
	p-hexanal
	n-heptanal
	n-octanal
	n-nonanal
	undecanal
	dodecanal
	benzaldehyde
	dimethylbenzaldehyde
	acetone
	methylisopropyl ketone
	butanone
	1-phenyl-1-propanone
	2-pentanone
	o-hydroxyacetophenone
	m-hydroxyacetophenone
	benzophenone
	9-fluorenone
	benzofluorenone
	dihydroxyanthraquinone
	tetrahydroanthraquinone
	phenanthridone
8. Carboxylic Acids and Derivatives	phthalic acids
	phthalic esters
	adipate esters
	phthalate esters
	$>C_9$ aliphatic esters
	acetic acid
	benzoic acid
	benzamide
	ethyl acetate
	ethylbenzyl acetate
	methyl benzoate
	isobutyl cinnamate
	dibutyl phthalate (artifact)
	diisobutyl phthalate (artifact)
	dicyclohexyl phthalate (artifact)
9. Nitriles	cyanotoluene (benzonitrile)
	acetonitrile
	cyanobutadiene
	2,2′-dicyanobiphenyl
10. Amines	aniline
	C_2-alkylaniline
	C_3-alkylaniline
	aminotoluene
	benzofluoreneamine
	methylaminoacenaphthylene
	methybenzofluoreneamine
	benzidine
	1-aminonaphthalene
	methylaminonaphthalene
	aminotetralin
	diphenylamine
	N-methyl-o-toluidine
13. Thiols, Sulfides, and Disulfides	methanethiol
	ethanethiol
	propylenethiol
	2,3,4-trithiapentane
	dimethyl sulfide
	dimethyl disulfide
	trithiahexane
	diphenyl disulfide
15. Benzene, Substituted	Benzene Hydrocarbons
	benzene
	C_2-alkylbenzene
	C_3-alkylbenzene
	toluene
	ethylbenzene
	styrene
	C_3-benzene
	C_4-benzene
	biphenyl
	biphenylene
	diphenylmethane
	indan
	C_2-alkylindane
	C_3-alkylindane
	methylindane
	xylenes
	o-xylene
	m- and p- xylene
	xylene and ethyl benzene
	tetrahydronaphthalene
	methylstyrene
	ethylstyrene
	n-propylbenzene
	isopropylbenzene
	1,2-dimethylbenzene
	t-butylbenzene
	n-pentylbenzene
	3,5-dimethyl-1-isopropylbenzene
	triethylbenzene
	o-ethyltoluene
	m-ethyltoluene
	trimethylbenzene
	1,2,4-trimethylbenzene
	1,3,5-trimethylbenzene
	o-diethylbenzene
	m-diethylbenzene
	p-diethylbenzene

TABLE 1 (continued).

MEG Category	Name
15. (Continued)	
	methyltetrahydronaphthalene
	dimethyltetrahydronaphthalene
	trimethyltetrahydronaphthalene
	1,2,3,4-tetrahydronaphthalene
	5,8-dimethyl-1-n-octyl-1,2,3,4-tetrahydronaphthalene
	1-methyl-4-n-heptyl-1,2,3,4-tetrahydronaphthalene
	methylbiphenyl
	3-methylbiphenyl
	diphenylethane
	di(ethylphenyl)ethane
	stilbene(1,2 diphenylethene)
	methylphenylethyne
	diphenylethyne
	1,2-diphenylpropane
	dixylylethane
	o-terphenyl
	m-terphenyl
	p-terphenyl
	dimethylindan
	pentamethylindan
	methy-1,2,3-dihydroindene
	dimethylindene
	trimethylindene
16. Polychlorinated biphenyls (PCB)	
	none
17. Dinitrotoluenes	
	none
18. Phenols	
	phenols
	C_2-alkylphenol
	C_3-alkylphenol
	C_4-alkylphenol
	isopropylphenol
	n-propylphenol
	cresol
	xylenol
	2,4,6-trimethylphenol
	1-naphthol
	1-acenaphthol
	C_2-alkylacenaphthol
	C_3-alkylacenephthol
	C_2-alkylhydroxyacenaphthene
	C_5-alkylhydroxyanthracene
	C_2-alkylhydroxypyrene
	C_2-alkylnaphthol
	hydroxyacenaphthene
	hydroxyanthracene
	hydroxybenzofluorene
	methylacenaphthol
	methylnaphthol
	indanol
18. (Continued)	
	o-cresol
	m-cresol
	p-cresol
	o-ethylphenol
	m-ethylphenol
	p-ethylphenol
	o-allylphenol
	m-phenylphenol
	2,3-xylenol
	2,4-xylenol
	2,5-xylenol
	2,6-xylenol
	3,4-xylenol
	3,5-xylenol
	3-methyl-6-ethylphenol
	2-methyl-4-ethylphenol
	4-tert-butyl-o-cresol
	di-t-buytl-4-ethylphenol
	trimethylphenol
	2-hydroxynaphthalene
	methylhydroxynaphthalene
	hydroxyfluorene
20. Dinitrocresol	
	none
21. Fused Polycyclic Hydrocarbons	
	naphthalene
	higher aromatics
	methylnaphthalene
	1-methylnaphthalene
	2-methylnaphthalene
	C_2alkylnaphthalene
	anthracene
	C_2-alkylanthracene
	9-methyl anthracene
	phenanthrene
	acenaphthene
	acenaphthylene
	C_2-alkylacenaphthalene
	C_2-alkylacenaphthene
	C_3-alkylacenaphthene
	binaphthyl
	methylacenaphthylene
	methylacenaphthene
	$C_{15}H_{12}$:3 rings
	benzo(a)anthracene
	7,12-dimethylbenzo(a)anthracene
	methyl phenanthracene
	methyltriphenylene
	triphenylene
	$C_{16}H_{10}$:4 rings
	3-methylcholanthrene
	benzo(c)phenanthrene
21. (Continued)	
	chrysene
	methyl crysene
	pyrene
	1-methyl pyrene
	dibenz(a,h)-anthracene
	benzo(a)pyrene
	perylene
	benzo(e)pyrene
	benzoperylene
	benzo(g,h,i)perylene
	cyclobutadibenzene
	methyldihydronaphthalene
	ethylnaphthalene
	isopropylnaphthalene
	1-methyl-7-isopropylnaphthalene
	1,2-dihydro-3,5,8-trimethylnaphthalene
	2-benzylnaphthalene
	dimethylnaphthalene
	1,4-dimethylnaphthalene
	2,3-dimethylnaphthalene
	2,6-dimethylnaphthalene
	trimethylnaphthalene
	3-methylacenaphthalene
	ethylanthracene
	1-methylphenanthrene
	3-methylphenanthrene
	4,5-methylphenanthrene
	propenylphenanthrene
	trans-9-propenylphenanthrene
	8-n-butylphenanthrene
	2,7-dimethylphenanthrene
	1,2-benzanthracene
	hexahydro-1,2-benzanthracene
	methyl-1,2-benzanthracene
	2,3-benzanthracene (naphthacene)
	3,4-benzophenanthrene
	methylbenzophenanthrene
	5,8-dimethyl-3,4-benzophenanthrene
	9,10-benzophenanthrene (triphenylene)
	1,2,3,4-tetrahydro-9,10-benzophenanthrene
	2-methyl-9,10-benzophenanthrene
	2-n-hexyperylene

Table 1 (continued).

MEG Category Name

22. Fused Non-Alternant Polycyclic Hydrocarbons
    - indene
    - C_2-alkylindene
    - C_3-alkylindene
    - fluorene
    - methylindene
    - methylfluorene
    - benzofluorene (fluoranthene)
    - benzo(b)fluorene
    - benzo(a)fluorene
    - benzo(k)fluoranthene
    - benzo(b)fluoranthene
    - indeno(1,2,3-cd)pyrene

    - 1-methylfluorene
    - dimethylfluorene
    - 1,2,3,4-tetrahydrofluoranthene

23. Heterocyclic Nitrogen Compounds
    - pyridine
    - C_2-alkylpyridine
    - C_3-alkylpyridine
    - C_4-alkylpyridine
    - methylpyridine (picolines)
    - dimethylpyroline
    - quinolines
    - C_2-alkylquinolines
    - C_3-alkylquinolines
    - 2-methylquinoline
    - acridine
    - C_3-alkylacridine
    - C_2-alkylacridine
    - C_2-alkylbenzoquinoline
    - C_3-alkylbenzoquinoline
    - methylacridine
    - dihydroacridine
    - methylbenzophenanthradine
    - benzophenanthridine
    - benzoquinoline (phenanthridine)
    - methylbenzoquinoline
    - indole
    - methylindole
    - carbazole
    - methylcarbazole
    - pyrroline

    - pyrrole
    - methylpyrrole
    - 4-acetylpyridine
    - trimethylpyridine
    - 2,4-dimethyl-6-ethylpyridine

23. (Continued)
    - 2-hydroxy-4-phenylpyridine
    - 2-hydroxy-6-phenylpyridine
    - 3,4-diphenylpyridine
    - benzopyridine
    - 2,2′-dimethyl-4,4′-dipyridyl
    - methyl-3-allylhydroindole
    - 3-methyl-3-allydihydroindole
    - phenylindole
    - 3-methyl-2-phenylindole
    - 3,3′-biindolyl
    - isoquinoline
    - 3-methylquinoline
    - 6-methylquinoline
    - ethylquinoline
    - 3-n-propylquinoline
    - 4-n-propylquinoline
    - 8-n-propylquinoline
    - dimethylquinoline
    - 2,6-dimethylquinoline
    - methylphenylquinoxaline
    - 4-styrylquinoline
    - 3-methylbenzoquinoline
    - benzimidazole
    - methylbenzimidazole
    - 2-ethylbenzimidazole
    - benzylbenzimidazole
    - benzothiazole
    - 2-methyl-5-phenyltetrazole
    - diphenyloxazole
    - dimethylacridine
    - acridone
    - 1,2,3,4-tetrahydrocarbazole
    - 3-amino-9-ethylcarbazole
    - vinylphenylcarbazole
    - 1,4-dihydro-2,3-benzo(b)carbazole
    - 2-amino-4-phenyl-6-methyl-pyrimidine
    - 2-amino-5-chloro-4,6-dimethylpyrimidine
    - 4-(1,2,3,4-tetrahydro-2-naphthyl)-morpholine
    - 3-benzylindene phthalimide

24. Heterocyclic Oxygen Compounds
    - methyldioxolane
    - benzofuran
    - dibenzofuran

24. (Continued)
    - furan
    - 2-methylbenzofuran
    - 3-methylbenzofuran
    - 5-methylbenzofuran
    - 7-methylbenzofuran
    - 3,3-dihydro-2-methylbenzofuran
    - dimethylbenzofuran
    - 3,6-dimethylbenzofuran
    - dihydromethylphenylbenzofuran
    - xanthene

25. Heterocyclic Sulfur Compounds
    - thiophene
    - C_2-thiophenes
    - methylthiophene
    - dimethylthiophene
    - benzothiophene

    - trimethylthiophene
    - isopropylthiophene
    - ethylthiophene
    - 2-n-propyl-5-isobutylthiophene
    - methylbenzothiophene
    - dimethylbenzothiophene
    - trimethylbenzothiophene
    - benzodithiophene
    - methylbenzodithiophene
    - dibenzothiophene
    - methyldibenzothiophene
    - dihydrodimethylthienothiophene
    - dimethylthiaindene
    - thiaxanthene

Note: Compounds are listed by MEG category with those which have been quantitated followed by those for which qualitative identifications are available.

TABLE 2. MAXIMUM CONCENTRATIONS REPORTED FOR GASEOUS STREAMS FROM COAL GASIFICATION ($\mu g/m^3$)

Gas (Product)			Gas (Discharge)		
Carbon Dioxide	4.7E8	RTI	Carbon Dioxide	1.1E9	K
Carbon Monoxide	3.0E8	RTI	Ammonia	3.2E8	K
Methane	3.6E7	RTI	C_6+ hydrocarbons	2.9E8	K
Hydrogen	2.7E7	RTI	Benzene	1.3E8	K
Hydrogen Sulfide	1.7E7	RTI	Methane	5.4E7	K
Benzene	3.3E6	RTI	Hydrogen Sulfide	3.0E7	K
Thiophene	2.3E6	RTI	Ethanethiol	2.7E7	K
Toluene	1.3E6	RTI	Phenols	2.6E7	K
Ethane	1.3E6	RTI	Ethane	2.1E7	K
Ethylene	9.4E5	RTI	Methanethiol	1.1E7	K

RTI = Research Triangle Institute.

K = Kosovo Gasification Plant.

TABLE 3. MAXIMUM CONCENTRATIONS REPORTED FOR LIQUID DISCHARGES FROM COAL GASIFICATION (μg/ℓ)

Organics			Inorganics		
Phenol	2.8E6	RTI	Ammonia	7.9E6	RTI
Cresols	1.5E6	RTI	Sulfate	2.8E6	Ft. Snlg.
Xylenols	3.75E5	RTI	Sodium	1.7E6	Ft. Snlg.
2,4,6-Trimethylphenol	1.8E4	RTI	Cyanide	1.0E6	RTI
1-Methylnaphthalene	4.8E2	RTI	Sulfur	9.7E5	Ft. Snlg.
2-Methylnaphthalene	2.2E2	RTI	Thiocyanate	2.7E5	RTI
Chrysene	1.6E2	RTI	Calcium	2.2E5	Ft. Snlg.
Phenanthrene	9.6E1	RTI	Sulfite	4.7E4	Ft. Snlg.
Acenaphthene	5.7E1	RTI	Sulfite	4.7E4	Ft. Snlg.
Fluorene	5.7E1	RTI	Nitrate	1.7E4	GG

RTI = Research Triangle Institute.

GG = Glen Gery Gasification Plant.

TABLE 4. MAXIMUM CONCENTRATIONS REPORTED FOR SELECTED COAL GASIFICATION STREAMS (μg/g)

Solid (Discharge)			Tar (Byproducts)		
Potassium	4.0E5	Chapman	Xylenols	1.2E5	RTI
Silicon	1.4E5	Ft. Snlg.	Cresols	6.7E4	RTI
Iron	9.0E4	Ft. Snlg.	Naphthalene	5.7E4	RTI
Aluminum	8.8E4	Ft. Snlg.	Benzofluorene	3.4E4	RTI
Calcium	5.0E4	Ft. Snlg.	Phthalate Esters	3.0E4	Chapman
Rubidium	2.0E4	Chapman	2,4,6-Trimethylphenol	2.4E4	RTI
Sodium	1.8E4	Ft. Snlg.	Pyrene	2.4E4	RTI
Sulfur	1.5E4	GG	Phenanthrene	2.3E4	RTI
Magnesium	1.3E4	Ft. Snlg.	Anthracene	2.3E4	RTI
Barium	5.5E3	Ft. Snlg.	Phenols	2.2E4	RTI

RTI = Research Triangle Institute

GG = Glen Gery Gasification Plant.

maxima are tabulated without regard to stream flow rate or potential dilution effects, as such they represent a measure of potential acute exposure hazard. Long-term effects may be gauged more realistically by consideration of actual mass emissions.

For each source considered, the mass flow rates in all product, byproduct and discharge streams were summed for each chemical species quantitated. These sums were then normalized by dividing by the coal input rate for each source to obtain production factors. Process streams which do not leave the facility were excluded from this analysis to avoid counting the same material more than once as it moves through the gasification facility. For the 14 source compilations (four from Radian plus 10 from RTI) maximum production factors for each chemical species quantitated were determined. These factors are listed in Table 5 accompanied by an entry referring to the source upon which they are based. While those values have been normalized on the basis of coal input, it must be remembered that different streams were sampled at different locations and different chemical analytical strategies were adopted for different samples.

Priorities for monitoring, regulation, and control technology development may be established from a ranking of the potential hazards associated with individual chemical species. Discharge severity can be used for this purpose. Table 6 lists those species of potential health hazard. Discharge severities of less than one represent minimal hazards; species in this category have been omitted from the table. The remaining species are ranked by the order of magnitude of their discharge severity. Primary consideration should be given to controlling those species occupying the highest positions on the list.

A similar ranking is presented in Table 7. Here, ecological DMEG values have been used in the calculation of discharge severities. Considerable differences in pollutant rankings occur between the two tables; a rational approach to pollutant control would emphasize the entries of highest discharge severity on both bases.

DISCUSSION

The processing of coal to yield gaseous fuels generates substances which are known to be hazardous. Among the wide spectrum of products, byproducts, process intermediates and waste streams are substances noted

TABLE 5. MAXIMUM TOTAL PRODUCTION FACTORS FOR CHEMICAL SPECIES DETERMINED IN MEASURED PRODUCT, BYPRODUCT AND DISCHARGE STREAMS FROM COAL GASIFIERS

MEG Category	Chemical Name	Production Factor (µg/g coal input)	
01A	Methane	1.2E5	R41
01A	Ethane	3.4E3	R21
01A	Propane	4.2E2	R21
01A	n-Butane	1.7E2	R21
01A	i-Butane	1.7E2	R21
01A	Pentanes	1.2E-6	K
01A	C_6 Alkanes	4.9E1	C
01A	$>C_{13}$ Alkanes	9.2E1	C
01A/B	Ethane & Ethylene	1.0E-7	K
01B	Ethylene	2.4E3	R21
01B	Propylene	4.9E2	R21
01C	Acetylene	3.1E1	R21
01C	Phenylacetylene	2.5E-1	C
03A	Anisoles	8.4E2	C
03A	Methylanisole	3.5E-1	C
05A	$>C_6$ Aliphatic Alcohols	3.4E2	C
05A	$>C_{13}$ Aliphatic Alcohols	6.2E-2	C
07B	Acetophenone	3.2E-2	C
08A	Phthallic Acid*	1.0E1	C
08D	Phthallic Esters*	3.0E3	C
08D	Adipate Esters	2.2E3	C
08D	$>C_9$ Aliphatic Esters	4.8E2	C
09B	Benzonitrile	2.0E-1	C
09B	Cyanotoluene	1.6E-1	C
10C	Aniline	8.9E0	R21
10C	Benzidine	2.0E1	R23
10C	Aminonaphthalene	1.0E2	C
10C	Methylaminonaphthalene	1.1E-1	C
10C	Aminotetralin	9.0E1	C
10C	C_2-Alkylaniline	1.0E1	C
10C	C_3-Alkylaniline	2.0E1	C
10C	Benzofluoreneamine	6.0E1	C
10C	Methylbenzofluoreneamine	2.0E1	C
10C	Methylaminoacenaphthylene	2.0E1	C
10C	Aminotoluene	4.8E-1	C
13A	Methanethiol	7.8E1	R36
13A	C_2H_6S	1.0E2	R41
15A	Benzene	3.8E4	R35
15A	Toluene	2.2E3	R35
15A	Ethybenzene	2.3E2	R21
15A	Biphenyl	9.2E1	R41
15A	Diphenylmethane	6.5E0	R25
15A/B	C_3-Alkylbenzene	4.2E0	C
15A	Styrene	1.1E0	C
15B	Xylenes	8.0E2	R35
15B	Indan	4.4E1	R41
15B/A	C_3-Benzenes	1.2E2	R41
15B/A	C_4-Benzenes	8.4E2	R41
15B	Tetrahydronaphthalene	6.6E2	C
16A	Polychlorinated Biphenyls*	3.1E-2	FS
17A	Dinitrotoluenes	4.5E0	FS
18A	Phenol	1.6E3	R35
18A	Cresols	1.6E3	R50
18A	Xylenols	1.3E3	R35
18A	Trimethylphenol	1.7E2	R43
18A	O-Isopropylphenol	1.7E2	R51
18A	C_2-Alkylphenol	6.8E2	C
18A	C_3-Alkylphenol	1.0E2	C
18A	C_4- Alkylphenol	3.8E-1	C
18C	Indanol	3.0E1	C
18C	Naphthol	1.8E2	C
18C	Methylnaphthol	2.0E2	C
18C	C_2-Alkylnaphthol	3.0E1	C
18C	Hydroxyacenaphthylene	7.4E-3	C
18C	Hydroxyacenaphthene	3.0E1	C
18C	Methylhydroxyacenaphthene	9.0E1	C
18C	C_2-Alkylhydroxyacenaphthene	1.6E2	C
18C	C_3-Alkylhydroxyacenaphthene	7.0E1	C
18C	Hydroxyanthracene	1.5E2	C
18C	C_5-Alkylhydroxyanthracene	2.0E2	C
18C	C_2-Alkylhydroxypyrene	2.1E2	C
18C	Hydroxybenzofluorene	3.5E2	C
20B	Dinitrocresol	3.7E0	C
21A	Naphthalene	2.3E4	R21
21A	C_2-Alkylnaphthalene	5.0E2	C
21A	1-Methylnaphthalene	1.4E2	R25
21A	2-Methylnaphthalene	3.3E2	R21
21A	Acenaphthylene	4.3E2	C
21A	Acenaphthene	1.5E2	C
21A	Phenanthrene	7.6E2	R21
21A	9-Methylanthracene	5.3E2	R21
21A	Anthracene	6.9E2	R41
21A	$C_{15}H_{12}$: 3 rings	2.0E-1	R35
21A	Binaphthyl	2.8E-1	C
21A	Methylacenaphthylene	2.8E2	C
21A	Methylacenaphthene	6.3E1	C
21A	C_2-Alkylacenaphthene	1.2E2	C
21A	C_3-Alkylacenaphthene	5.1E1	C
21A	C_2-Alkylanthracene	8.0E1	C
21A	Higher Aromatics	6.9E-9	K
21B	Benz(a)Anthracene	1.6E2	R21
21B	Triphenylene	2.9E2	C
21B	Chrysene	2.9E2	C
21B	Pyrene	7.2E2	R41
21B	$C_{16}H_{10}$: 4 rings	4.3E-1	R35
21B	7,12-Dimethylbenz(a) Anthracene	3.3E-1	FS
21B	3-Methylcholanthrene	9.6E-3	FS
21B	Benzo(c)Phenanthrene	2.0E0	FS
21B	Methylphenanthracene	2.1E2	C
21B	Methylchrysene	5.4E2	C
21B	Methylpyrene	3.8E2	C
21B	Methyltriphenylene	1.2E2	C
21C	Dibenzo(a,h)Anthracene	9.3E1	R21
21C	Benzo(a)Pyrene	1.2E2	R21
21C	Benzo(e)Pyrene	6.9E1	R21
21C	Perylene	8.0E1	C
21D	Benzo(g,h,i)Perylene	4.8E1	R25
21D	Benzoperylene	5.0E1	C
22A	Fluorene	2.6E2	R21
22A	Indene	4.4E2	R41
22A	Methylindene	1.5E1	C
22A	C_2 Alkylindene	3.7E1	C
22A	C_3 Alkylindene	1.4E0	C
22B	Benzo(a)Fluorene	8.6E1	R21
22B	Benzo(b) Fluorene	5.6E1	R21
22B	Fluoranthene	1.0E3	R41
22B	Benzofluorene	3.8E2	C
22C	Benzo(h)Fluoranthene	5.3E1	R21
22C	Benzo(b)Fluoranthene	1.0E2	R21

TABLE 5. MAXIMUM TOTAL PRODUCTION FACTORS FOR CHEMICAL SPECIES DETERMINED IN MEASURED PRODUCT, BYPRODUCT AND DISCHARGE STREAMS FROM COAL GASIFIERS (continued)

MEG Category	Chemical Name	Production Factor (μg/g coal input)		MEG Category	Chemical Name	Production Factor (μg/g coal input)	
22D	Indeno(1,2,3-CD)Pyrene	4.6E1	R21	48	Phosphate	9.6E1	GG
23A	Pyridine	1.6E-1	C	49	Arsenic	2.7E1	GS
23A	Methylpyridine	7.1E-1	C	50	Antimony	1.3E1	C
23A	C_2-Alkylpyridine	2.8E0	C	51	Bismuth	1.7E0	GG
23A	C_3-Alkylpyridine	1.2E1	C	53	Sulfur	7.6E3	FS
23A	C_4-Alkylpyridine	2.0E1	C	53	Sulfate	7.0E1	FS
23B	Quinoline	1.9E3	C	53	Sulfite	1.2E0	FS
23B	Acridine	9.0E1	C	53	Hydrogen Sulfide	4.1E4	R25
23B	Methylquinoline	6.0E1	C	53	Carbonyl Sulfide	1.3E3	R50
23B	C_2-Alkylquinoline	2.3E2	C	53	Carbon Disulfide	2.8E2	R50
23B	C_3-Alkylquinoline	1.1E2	C	53	Sulfur Dioxide	1.7E0	C
23B	Methylacridine	4.0E1	C	53	Thiocyanate	5.9E2	R21
23B	Benzophenanthridine	9.6E-2	C	54	Selenium	4.4E1	FS
23B	Methylbenzophenanthridine	4.8E-2	C	55	Tellurium	2.0E-2	GG
23B	C_2-Alkylacridine	9.0E1	C	56	Fluorine	1.7E2	FS
23B	C_3-Alkylacridine	6.0E1	C	56	Fluoride	5.9E0	GG
23B	Benzoquinoline	7.0E1	C	57	Chlorine	4.8E3	R21
23B	Methylbenzoquinoline	3.0E2	C	57	Chloride	2.8E3	R50
23B	C_2-Alkylbenzoquinoline	6.0E1	C	58	Bromine	2.9E1	GG
23B	Dihydroacridine	2.2E-1	FS	58	Bromide	5.8E-1	C
23C	Indole	1.9E0	R21	59	Iodine	5.0E1	GG
23C	Carbazole	5.3E1	R50	59	Iodide	5.0E-2	R50
23C	Methylcarbazole	2.0E1	C	60	Scandium	3.5E0	FS
23C	Pyrroline	4.0E-2	C	61	Yttrium	5.0E1	FS
24A	Benzofuran	1.3E2	R25	62	Titanium	3.8E3	FS
24B	Dibenzofuran	2.7E2	R21	63	Zirconium	1.5E2	FS
25A	Thiophene	3.7E3	R51	64	Hafnium	8.6E-1	FS
25A	Methylthiophene	2.9E2	R41	65	Vanadium	3.5E2	FS
25A	Dimethylthiophene	5.0E1	R41	66	Niobium	2.6E1	FS
25A	C_2-Thiophenes	3.3E2	R23	68	Chromium	5.5E2	R50
25B	Benzothiophene	2.6E2	R41	69	Molybdenum	1.4E1	GG
27	Lithium	4.1E1	FS	70	Tungsten	8.7E-1	FS
28	Sodium	1.5E4	FS	71	Manganese	1.9E2	FS
29	Potassium	7.3E3	FS	72	Iron	7.6E4	FS
30	Rubidium	1.2E3	C	72	Iron Carbonyl**	1.1E0	GG
31	Cesium	6.8E0	FS	74	Cobalt	2.0E1	FS
32	Beryllium	7.6E0	FS	76	Nickel	6.4E1	FS
33	Magnesium	1.1E4	FS	76	Nickel Carbonyl**	2.0E-4	GG
33	Rhenium	6.1E-1	FS	78	Copper	1.0E2	C
34	Calcium	4.4E4	FS	79	Silver	8.1E-1	FS
35	Strontium	1.6E3	FS	80	Gold	8.6E-4	GG
36	Barium	4.7E3	FS	81	Zinc	2.0E1	FS
37	Boron	1.8E2	FS	82	Cadmium	6.9E1	FS
38	Aluminum	7.5E4	FS	83	Mercury	1.4E1	FS
39	Gallium	8.0E0	FS	84	Cerium	9.3E1	FS
41	Thallium	4.8E-2	GG	84	Lanthanum	9.3E1	FS
42	Carbon Monoxide	9.8E5	R48	84	Neodymium	2.5E1	FS
42	Carbon Dioxide	1.2E6	R48	84	Praseodymium	1.4E1	FS
42	Carbonate	3.5E-4	C	84	Samarium	1.1E1	FS
43	Silicon	4.3E2	C	84	Dysprosium	1.2E-2	FS
44	Germanium	1.1E-1	FS	84	Erbium	1.3E-3	FS
45	Tin	1.8E1	C	84	Europium	2.0E-3	FS
46	Lead	1.1E1	R50	84	Gadolinium	3.9E-3	FS
47	Ammonia	8.8E3	R21	84	Holmium	2.0E-3	FS
47	Cyanide	2.1E1	R48	84	Terbium	6.8E-2	GG
47	Nitrogen Oxide	7.3E0	C	84	Thulium	1.9E-2	GG
47	Nitrogen Dioxide	5.3E1	C	84	Lutetium	2.9E-2	GG
47	Nitrate	2.2E-2	R21	84	Ytterbium	1.9E-1	GG
47	Nitrite	5.0E-4	FS	85	Thorium	2.0E1	FS
48	Phosphorus	1.7E3	FS	85	Uranium	1.4E1	FS

* Probable Artifact
** Inferred Concentration

C = Chapman
FS = Wellman Galusha (Fort Snelling)
GG = Wellman Galusha (Glen Gery)
K = Kosovo
R( ) = RTI (Test Number)

TABLE 6. RANKING OF CHEMICAL SPECIES IN COAL GASIFICATION STREAMS RELATIVE TO THEIR ENVIRONMENTAL (HEALTH) HAZARD POTENTIAL)

Discharge Severity (Order of Magnitude)	Stream Type			
	Gaseous	Liquid	Solid	Tar
100,000	benzo(a)pyrene+(C,D)	cresols(R43,D)(R50,D) xylenols+(R50,D)		benzo(a)pyrene +(R21,P) cresols(R51,P) xylenols+(R43,P)
10,000	ammonia+(K,D) benzene+(K,D) carbon monoxide(G,D) ethanethiol(K,D) methanethiol(K,D)		chromium+(R43,D)***	dibenzo(a,h)anthracene+(R25,P) trimethylphenol(R43,P)
1,000	carbon dioxide(K,S) hydrogen cyanide+(K,D) hydrogen sulfide(R25,P) phenol+(K,D) chromium+(C,D) 7,12-dimethylbenz(a) anthracene(F,P) thiophene(R51,P)	ammonia+(R25,D) arsenic+(R50,D) chromium+(R50,D) *** cyanide+(C,S) mercury(K,S)	mercury+(G,D)	chromium+(R36,P)*** naphthol(C,P)
100	arsenic+(F,P) carbonyl sulfide(K,S) dibenzo(a,h)anthracene+(F,P) hydrogen(R21,P) iron carbonyl**(G,D) mercury+(F,P) selenium+(F,)P silver+(C,D) uranium(C,D)	benzo(a)pyrene+(R43,D) phenol+(R43,D)(R50,D) sodium(F,D)	arsenic+(R36,D) iron(F,D) potassium(C,D)	benzo(a)anthracene+(R25,P) indanol(C,P)
10	aluminum(F,P) aminotoluene(C,D) barium(F,P) benzo(a)anthracene+(F,P) biphenyl(F,P) cadmium+(F,P) calcium carbon disulfide(R50,P) copper+(C,D) cresols(C,D) C_4-hydrocarbons(K,S) C_5-hydrocarbons(K,D) dinitrocresols+(F,P) iron(F,P) lithium(F,P) magnesium(F,P) methane(R51,P) naphthalene+(R25,P) nickel+(F,P) nitrogen dioxide(C,D) phenanthrene+(C,D) phosphorus(F,P) phthalate esters*+(C,D) polychlorinated biphenyls (PCB)*+(F,P) potassium(C,D) sulfur dioxide(G,D) toluene+(K,D) xylenols+(R35,P)	fluoride(C,S) selenium+(C,S) sulfide(G,D)	aluminum(F,D) barium(F,D) beryllium+(R50,D) manganese+(G,D) nickel+(R51,D) selenium+(R43,D)	arsenic+(R51,P) phenol+(R51,P)
1	aminonaphthalene(C,D) benzo(c)phenanthrene(F,P) beryllium+(F,P) chrysene+(C,D) dinitrotoluene+(F,P) indene(C,D) lead+(C,D) 3-methylcholanthrene(F,P) nitrogen oxide(C,D) strontium(F,P) xylenes(R51,P)	aminotoluene(C,S) barium(G,D) iron(G,D) lead+(R50,D) lithium(F,D)(C,D) phosphorus(C,S) sulfate(F,D)	antimony+(C,D) calcium(F,D)(C,D) copper+(C,D) lead+(G,D) lithium(G,D) phosphorus(C,D) silicon(F,D)	aminotoluene(C,P) benzofluorenamine(C,P) benzo(b)fluoranthene(R21,P) biphenyl(R36,P) cadmium(R51,P) chrysene+(R25,P) copper(C,P) lead+(C,P) 9-methylanthracene(R21,P) phenanthrene+(R21,P)(R25,P) phthalate esters*+(C,P)

KEY

Source Gasifier		Source Stream Classification	
G	Wellman-Galusha (Glen-Gery)	D	Discharge
F	Wellman-Galusha (Ft. Snelling)	P	Product or Byproduct
C	Chapman	S	Process Stream
R#	RTI Run No.		
K	Kosovo Lurgi		

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*Probable artifact.

**Inferred from iron concentration.

***Stainless steel laboratory reactor probably resulted in increased concentration.

+Priority pollutant (consent decree compound).

TABLE 7. RANKING OF CHEMICAL SPECIES IN COAL GASIFICATION STREAMS RELATIVE TO THEIR ENVIRONMENTAL (ECOLOGY) HAZARD POTENTIAL

Discharge Severity (Order of Magnitude)	Stream Type			
	Gaseous	Liquid	Solid	Tar
1,000,000			phosphorus(C,D)	naphthalene(R21,P)+
100,000	ammonia(K,D) benzene(K,D) ethylene(K,S)	ammonia(C,S),(R25,D)+		cresols(R51,P) xylenol(R43,P)+
10,000		cyanide(C,S)+ phosphorus(C,S) phthalates(C,S)*+		benzidine(R23,P)+ phenol(R51,P)+ phthalate esters(C,P)*+ trimethylphenol(R43,P)
1,000	carbon monoxide(G,D) hydrogen sulfide(R25,P) toluene(K,S)+	cresols(R43,49,50,D) phenol(R32,D)+ phosphates(K,S) sulfide(C,S) xylenols(R50,D)+	copper(C,D)+ iron(F,D) mercury(G,D)+	acridine(R20,P) arsenic(R21,P)+ chromium(R36,P)+** o-isopropylphenol(R51,P)
100	hydrogen cyanide(K,D)+ mercury(F,P)+ vanadium(C,D)	arsenic(R49,D)+ C_2-alkylphenols(C,S) chromium(R26,D)+** copper(R49,D)+ naphthalene(C,S)+ sulfite(F,D)	aluminum(F,D) chromium(R26,D)+** silver(F,D)+	acenaphthene(R16,P)+ aniline(R20,P) cadmium(R51,P) copper(C,P)+ mercury(R46,P)+ selenium(R51,P)+
10	methane(R51,P)	aluminum(F,D) barium(G,D) boron(C,S) cadmium(R16,D) calcium(F,D) C_3-alkylphenols(C,S) $>C_6$-alkanes(C,S) iron(G&F,D) nitrates(G,D) selenium(C,S)+ silver(C,S,F&G,D)+ sulfate(F,D) thiocyanate(R21,D) titanium(G,D) trimethylphenol(R21,D)	arsenic(G,C)+ barium(F,D) calcium(C,D) cobalt(C,D) manganese(C,D)+ phthalate esters(C,D)*+ potassium(C,D) titanium(F,D) vanadium(F,D)	aminonaphthalene(C,P) aminotetralin(C,P) C_2-alkylacenaphthol(C,P) C_2-alkylbenzoquinoline(C,P) C_2-alkylhydroxypyrene(C,P) C_5-alkylhydroxyanthracene(C,P) cobalt(R52,P) hydroxyanthracene(C,P) hydroxybenzofluorene(C,P) manganese(R51,P)+ methylnaphthol(C,P) naphthol(C,P) nickel(R51,P)+ titanium(R52,P)
1	C_2-alkylbenzene(C,D) C_3-alkylbenzene(C,D) ethane(K,D) thiocyanate(C,D)	alkylpyridine(K,S) aniline(C,S) C_2-alkylaniline(C,S) dimethylpyridine(K,S) lead(K,S)+ lithium(G&F,D) mercury(K,S)+ 2-methylpyridine(K,S) 3&4-methylpyridine(K,S) pyridine(K,S) vanadium(G,D) zinc(K,S)+	antimony(C,D)+ boron(F,D) cadmium(C,D) lithium(G,D) nickel(R51,D)+ selenium(C,D)+ uranium(C,D)	acenaphthol(C,P) antimony(R49,P)+ C_2-alkylacridine(C,P) C_2-alkylnaphthol(C,P) C_2-alkylphenol(C,P) C_3-alkylacridine(C,P) C_3-alkylacenaphthol(C,P) C_3-alkylnaphthol(C,P) C_3-alkylphenol(C,P) C_3-benzoquinoline(C,P) $>C_9$-aliphatic esters(C,P) indanol(C,P) lead(R31,P)+ methylacenaphthol(C,P) methylacridine(C,P)

KEY

Source Gasifier	Source Stream Classification
G Wellman-Galusha (Glen-Gery) F Wellman-Galusha (Ft. Snelling) C Chapman R# RTI Run No. K Kosovo Lurgi	D Discharge P Product or Byproduct S Process Stream

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*Probable artifact.

**Stainless steel laboratory reactor probably resulted in increased concentration.

+Priority pollutant (consent decree compound).

for acute and chronic toxicity as well as substances capable of causing long-term ecological damage. Indeed, one of the major goals of low Btu gasification is the production of carbon monoxide, a well-known poison even at very low levels. Trace contaminants present in coal gasification streams include some materials considered very hazardous and some considered relatively benign, as well as a large number with unquantified health and ecological effects.

From the standpoint of potential health hazard, the gaseous pollutant having the highest discharge severity in an individual stream is benzo(a)-pyrene. Present at discharge severities an order of magnitude lower (10,000) but still extremely high were ammonia, benzene, carbon monoxide, ethanethiol and methanethiol. The concentrations of pollutants must be greatly reduced before any environmentally acceptable discharge can take place. Overall, 61 gaseous species were found at DS levels greater than one including 26 of the EPA priority pollutants.

Liquid pollutants representing the highest potential health hazards were cresols and xylenols. Technology exists for the recovery or treatment of these compounds. Ammonia, arsenic, chromium, cyanide, and mercury were found in liquid streams at levels two order of magnitude lower (DS = 1000) but still require high levels of control. Twenty-one species were found in liquid streams at discharge severities greater than one; these include 10 species on the EPA consent decree list.

In the solid streams, chromium (DS = 10,000), mercury (DS = 1,000), arsenic, iron and potassium (DS = 100) present the most serious health hazards. It is likely that ash and dust disposal methods will be devised to safely handle the overall material; no element specific treatment technology is available or promising. Eighteen species were found in solid streams at discharge severities exceeding one. These included 10 EPA priority pollutants.

The species present in tars which represent the highest potential health hazards are benzo(a)pyrene, cresols and xylenols (DS = 100,000). One order of magnitude less hazardous, dibenz(a,h)anthracene and trimethylphenol were found to be present. Some use for this byproduct material, perhaps involving combustion or gasification to produce more valuable chemicals may be feasible, eliminating or minimizing potential human exposure. Twenty-two species were found in the tar at DS levels greater than one. These included 11 EPA priority pollutants.

Potential ecological hazards were more severe in some cases than health hazards. Among the gas streams, three species: ammonia, benzene and ethylene were found at ecological discharge severity levels of 100,000. Phosphorus (solid phase) and naphthalene (tar) were found to have discharge severities of 1,000,000. Carbon monoxide, hydrogen sulfide and toluene were other ecologically hazardous pollutants in the gas phase (DS = 1000). Overall, 16 species were found in the gas phase at DS levels greater than one. (This listing includes species for which supplemental DMEG values were assigned). These included three EPA priority pollutants.

In the liquid phase, ammonia (DS = 10,000), and cyanide, phosphorus and phthalates (DS = 1000) were the most hazardous ecologically. Forty-two species were found in liquid streams at DS levels greater than one. These include 14 species on the EPA priority list.

In addition to phosphorus (DS = 1,000,000), copper, iron, and mercury (DS = 1000) were the most ecologically hazardous species in the solid streams. Twenty-three species were found in the solid streams at DS levels greater than one. Of these, 10 are on the EPA priority pollutant list.

Cresols and xylenols (DS = 100,000) were found in tars at DS levels one order of magnitude lower than naphthalene but still represent extremely high ecological hazards. In all, 46 species were found in tars with DS levels greater than one. These include 15 species on the EPA priority list.

Individual chemical species within the coal gasification streams considered in this analysis have been ranked in order of their potential hazards to health and ecology. Priorities for future monitoring and regulatory efforts can be developed on the basis of these rankings. Primary consideration must be given to expected discharges to the environment. Many product materials of an extremely hazardous nature can be used with minimal opportunities for human contact or ecological damage. Similarly, intermediates within process facilities may be more hazardous than either the starting material or the end product when considered strictly on the basis of chemical analysis. Actual efforts towards pollution control and towards the development of pollution control equipment must focus on eliminating hazardous discharges and minimizing fugitive emissions.

SUMMARY

The U.S. Environmental Protection Agency (EPA) has supported a number of research programs concerned with the environmental aspects of synthetic fuels production. An environmental assessment methodology has been applied to chemical data obtained from sampling and analysis of products, byproducts and effluents from a laboratory gasifier at Research Triangle Institute (RTI). In addition, data obtained during source tests of four operating coal gasifiers by the Radian Corporation have been similarly analyzed. Over 400 organic chemicals have been either quantitated or identified in samples obtained under these programs. Additionally, a large number of inorganic compounds and nearly all of the naturally occurring elements have been found.

Of the chemical species quantitated, 61 in the gas phase, 21 in the liquid phase, 18 in the solid phase and 22 in the tars were found at levels exceeding their health DMEG values in at least one sample. Other potentially hazardous species for which no DMEG values have been established may also be present. In addition a number of species in each phase were found at concentrations in excess of their ecology DMEG values.

The most serious hazards in the gas phase were ammonia, benzene, benzo(a)pyrene, carbon monoxide, ethanethiol, ethylene, and methanethiol. In the liquid phase ammonia, cresols, cyanide, phosphorus and xylenols were found to present the most serious hazards. The greatest hazards in the solid phase were phosphorus, chromium, copper, iron and mercury. Based on land DMEGs, the most serious pollutants in the tar were naphthalene, benzo(a)-pyrene, cresols, and xylenols.

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EFFECT OF SLUDGE AGE ON THE BIOLOGICAL TREATABILITY OF A SYNTHETIC COAL CONVERSION WASTEWATER

by

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Abstract

Aerobic biological processes appear to be the focal point of any overall scheme for treating coal conversion wastewaters since a significant number of the major constituents of these wastes are biodegradable. Accordingly, suitable design and operating criteria for biological treatment facilities need to be developed. The studies to be described in this paper have been conducted using a synthetic wastewater which was formulated to be representative, in its organic composition, of actual wastewaters from coal gasification and coal liquefaction processes. The wastewater contains twenty-eight organic compounds, inorganic nutrients, and pH-buffers.

The synthetic coal conversion wastewater was fed to several bench-scale activated sludge reactors, operated at different solids retention times (sludge ages). Effluents from the reactors were analyzed by gas chromatography and high performance liquid chromatography to assess the degree of removal of the various constituents in the raw feed, and to identify reaction products following biological treatment. Additionally, acute toxicity studies using fathead minnows were conducted to evaluate the biological impact of the treated wastewaters on aquatic life. Acute mammalian cytotoxicity and Ames mutagenicity analyses were also performed on the reactor effluents to assess their potential impact on human health. This paper presents selected results of some of these analyses.

EFFECT OF SLUDGE AGE ON THE BIOLOGICAL TREATABILITY OF A SYNTHETIC COAL CONVERSION WASTEWATER

INTRODUCTION

In order to evaluate the biological treatability of wastewaters generated during the course of coal gasification and coal liquefaction, a synthetic coal conversion wastewater was formulated and fed to several bench-scale activated sludge reactors. The composition of the synthetic wastewater is shown in Table 1; the basis for formulating the wastewater in this manner has been presented previously.[1,2] The synthetic wastewater contains twenty-eight organic compounds representing the major classes of organics identified in actual coal conversion wastewaters, and essentially all of the specific organic compounds which have been reported to be present at high concentrations are included. The theoretical total organic carbon (TOC) concentration of all the components is 4,636 mg/l. The high concentrations of pH-buffering agents were provided in order to avoid the operational problems reported earlier due to inadequate control of pH.[1] It is unlikely that pH control will be a problem in treating real coal conversion wastewaters in view of the abundant amounts of carbonate alkalinity in the real wastewaters.[3]

PROCEDURES

The synthetic wastewater was made up in 200-liter batches and stored in a stainless steel tank. Carbon-filtered Chapel Hill tap water was used as dilution water to which the twenty-eight constituents, shown in Table 1, were added. This was accomplished by adding appropriate quantities from concentrated stock solutions, prepared periodically from reagent-grade chemicals and stored under refrigeration until use. It was found that in order to prepare some of the concentrated solutions, an organic solvent was required to maintain solubility of the component organics. Accordingly, methanol was employed for this purpose. The TOC attributable to the methanol was approximately 140 to 200 mg/l. This represents a change in procedure from that reported in an earlier paper.[1]

A series of 25-liter biological reactors were fed the synthetic wastewater. The wastewater was introduced into each reactor by a variable-speed peristaltic pump. Some of the reactors were operated as chemostats, i.e. continuous-flow, completely-mixed activated sludge systems with no recycle of solids (biomass). For these systems, the solids residence time (SRT) or sludge age was equal to the hydraulic retention time (HRT). Detention times of 3, 5, 7.5, 10, 20, and 40 days were investigated during this phase of the study. The pumps feeding the 3- and 5-day reactors were operated continuously, while the pumps feeding the other reactors were activated by a clock which operated them for a pre-determined period once every half-hour. The other reactors were operated with sludge recycle, on a modified fill-and-draw basis. In these systems, the reactors were fed continuously or intermittently as described above, but the effluent line from the reactor was kept closed, allowing the volume of the mixed liquor to increase. At various times, the air supply to the reactors was turned off for a short time (usually 30 min.), allowing

Table 1. COMPOSITION OF SYNTHETIC COAL CONVERSION WASTEWATER

COMPOUND	CONCENTRATION, mg/l
1. Phenol	2000
2. Resorcinol	1000
3. Catechol	1000
4. Acetic Acid	400
5. o-Cresol	400
6. p-Cresol	250
7. 3,4-Xylenol	250
8. 2,3-Xylenol	250
9. Pyridine	120
10. Benzoic Acid	100
11. 4-Ethylpyridine	100
12. 4-Methylcatechol	100
13. Acetophenone	50
14. 2-Indanol	50
15. Indene	50
16. Indole	50
17. 5-Methylresorcinol	50
18. 2-Naphthol	50
19. 2,3,5-Trimethylphenol	50
20. 2-Methylquinoline	40
21. 3,5-Xylenol	40
22. 3-Ethylphenol	30
23. Aniline	20
24. Hexanoic Acid	20
25. 1-Naphthol	20
26. Quinoline	10
27. Naphthalene	5
28. Anthracene	0.2
THEORETICAL ΣTOC ==	4636 mg/l
NH_4Cl (1000 mg/l as N)	3820
$MgSO_4 \cdot 7H_2O$	22.5
$CaCl_2$	27.5
$NaHCO_3$	300
FeNaEDTA	0.34
PHOSPHATE BUFFER: KH_2PO_4	852
K_2HPO_4	2176
$Na_2HPO_4 \cdot 7H_2O$	3340

the solids (biomass) in the reactor to settle. A portion of the supernatant liquor was then withdrawn from the reactor, and the volume and solids content of the remaining mixed liquor was adjusted to provide the desired hydraulic detention times and solids residence times. Other details describing the design and operation of the reactors have been reported previously.[1,2]

It should be noted that there was a significant color change in the synthetic feed solution, from clear to amber to brown, over the several days during which it was used to feed the reactors. Attempts were made to evaluate possible changes in wastewater composition during this time through periodic measurements of TOC and chromatographic scans using high performance liquid chromatography (HPLC). No changes in TOC were detected and the chromatographic analyses established that, while some changes do occur, these changes appear to be minimal.

Routine sampling of each reactor was performed three times a week. Parameters measured included temperature, pH, dissolved oxygen, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), and total organic carbon (TOC). Other samples were collected as desired for the measurement of biochemical oxygen demand (BOD) and chemical oxygen demand (COD), and for more detailed analysis including analyses for specific organic compounds using HPLC and GC/MS, aquatic toxicity, and assessment of potential human health effects.

RESULTS OF REACTOR PERFORMANCE

Figure 1 illustrates the failure of the biological systems to treat the full-strength synthetic wastewater. Both the chemostat and recycle systems, with solids retention times of 20 and 40 days, respectively, failed almost immediately despite attempts to gradually acclimatize the microorganisms to the wastewater. A second attempt was made by reducing the ammonia content of the synthetic feed to 250 mg/l as N in order to avoid potential ammonia toxicity, but again the reactors failed.

In order to overcome the possibility of toxicity due to other constituents of the synthetic wastewater, the synthetic feed was diluted to 25% of that shown in Table 1. Other investigators[4,5] have had to resort to similar dilution procedures in order to treat coal conversion wastewaters biologically. The resulting diluted version has a theoretical TOC of 1,159 mg/l, making it comparable to wastewaters used in biotreatability experiments being conducted by others.

Figures 2 through 6 demonstrate the performance of the 5-, 7.5-, 10-, 20-, and 40-day chemostats treating the quarter-strength synthetic wastewater. It is obvious that the gross toxicity effects observed for the full-strength wastewater have been overcome. The effluent TOC, in general, decreases with increasing retention time, reflecting improved treatment efficiency. (The influent TOC during this period of operation was measured to be 1,040 ±120 mg/l.) It should be noted that the scales for each of the figures are not the same, so that care must be exercised in comparing the results. No difficulties were encountered in controlling pH due to the high buffer intensity of the raw feed; the pH held steady at 6.9 to 7.4 compared to difficulties experienced in earlier studies.[1]

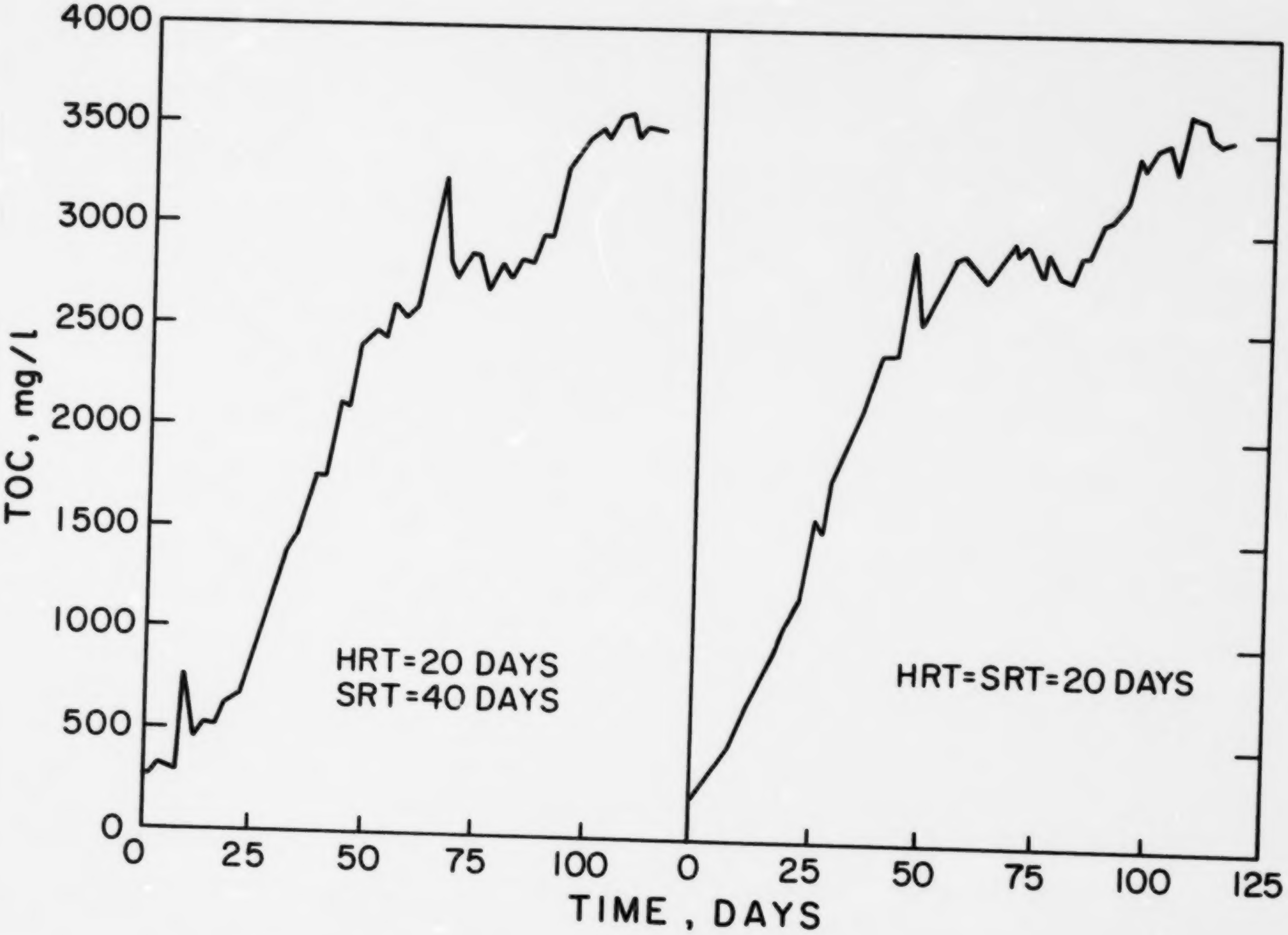

Figure 1. Failure of biological reactors to treat full-strength synthetic wastewater.

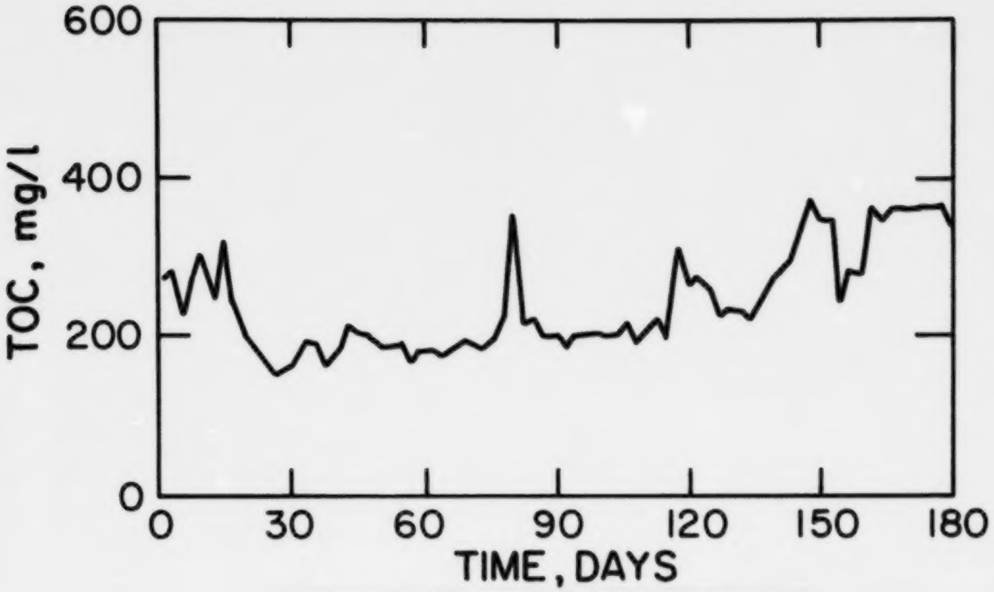

Figure 2. Effluent TOC from 5-day reactor.

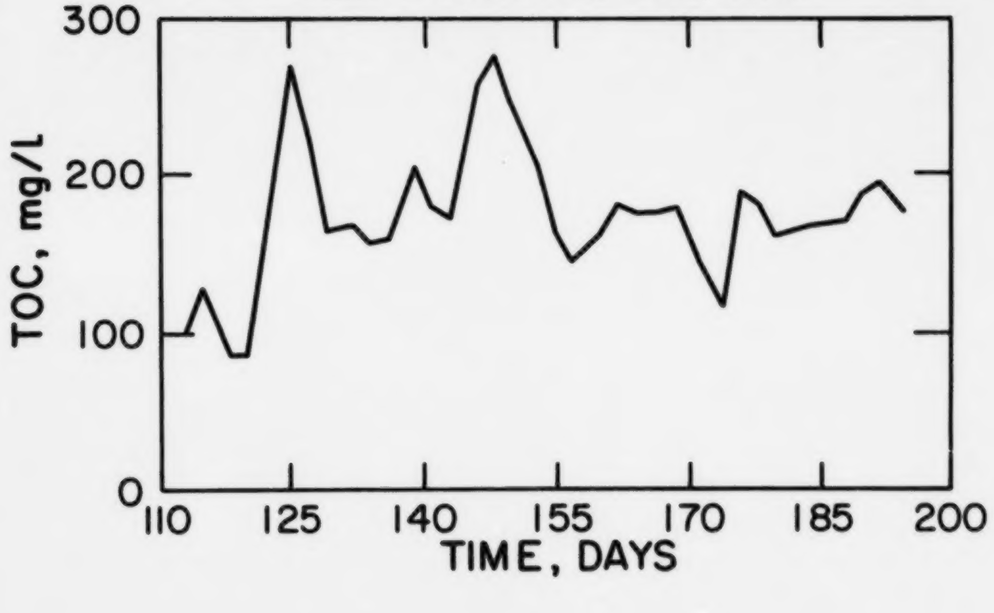

Figure 3. Effluent TOC from 7.5-day reactor.

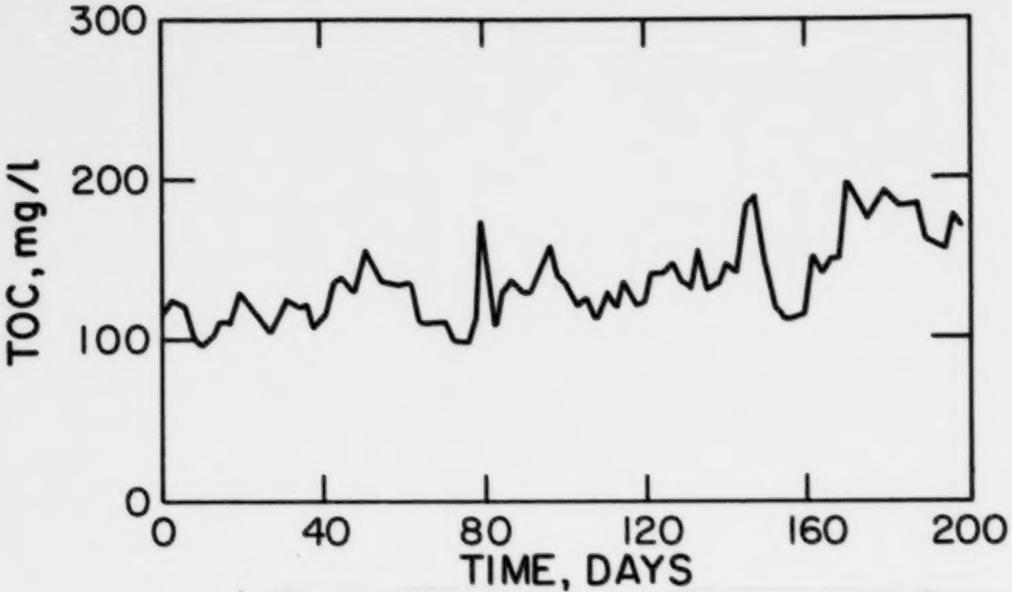

Figure 4. Effluent TOC from 10-day reactor.

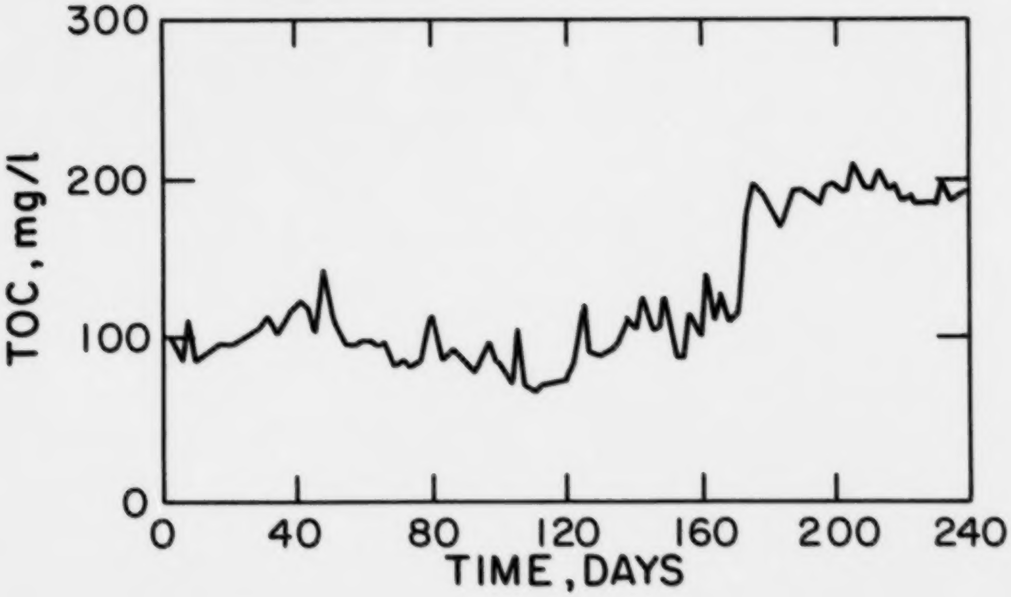

Figure 5. Effluent TOC from 20-day reactor.

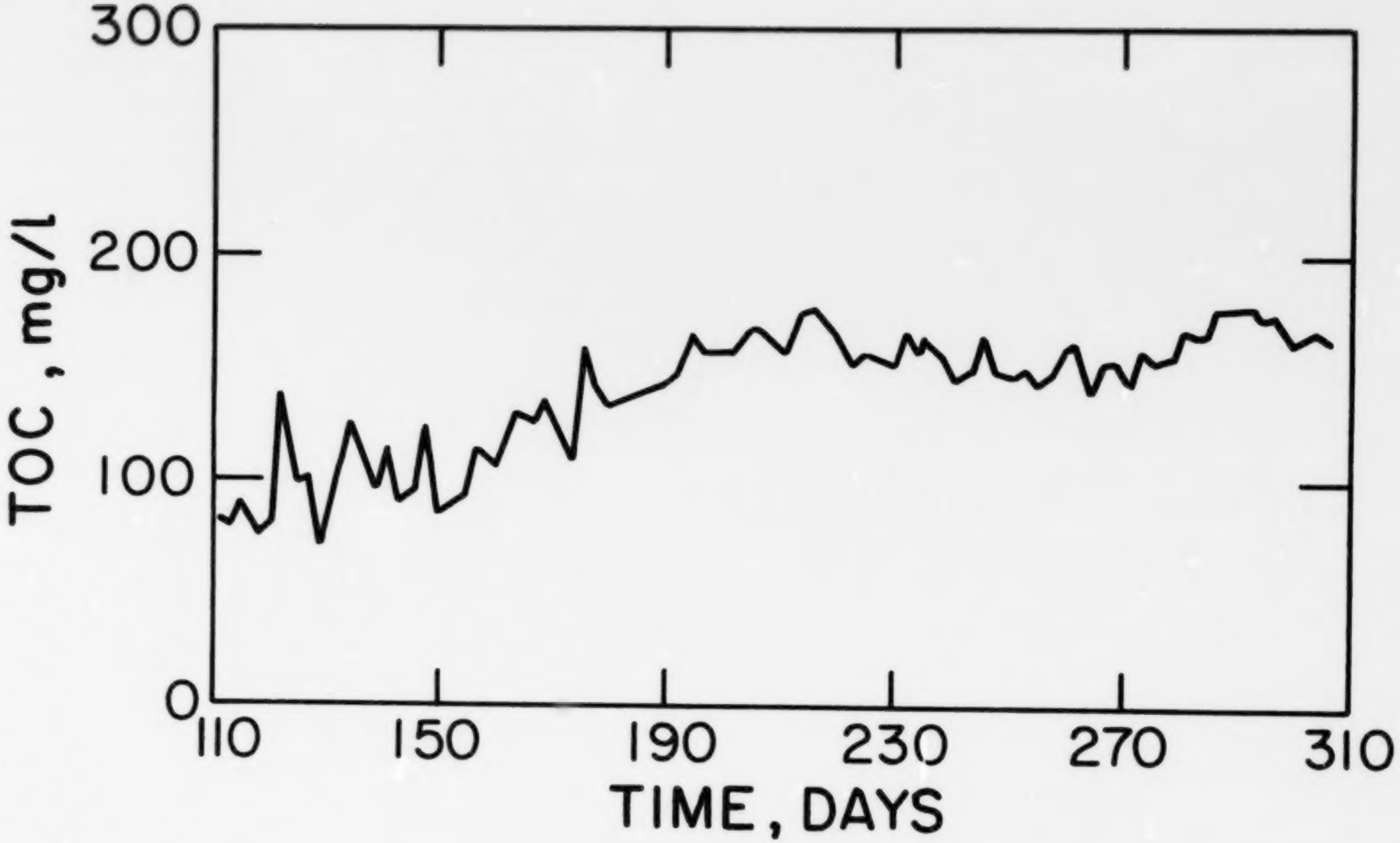

Figure 6. Effluent TOC from 40-day reactor.

Attempts to treat the quarter-strength wastewater with a 3-day residence time failed. Immediately after feeding of the 3-day reactor commenced, the effluent TOC began to rise and within a few days approached the influent TOC. This pattern was observed a second time, implying that the wastewater cannot be treated with such a low solids residence time.

A closer look at the TOC data in Figures 2 through 6 shows that, in general, reasonably steady performance was maintained for about 130 to 170 days, after which the effluent TOC increased somewhat. In fact, there appears to be a slight upward trend in the TOC data over the entire period of observation. Accordingly, it may be inappropriate to speak of steady-state behavior, despite the rather consistent performance of the reactors over this long observation period. Some of the observed fluctuations in TOC may be attributed to mechanical difficulties which were encountered at various times during this period of reactor operation. These included failures of the air compressor, feed pumps, and timing devices leading to occasional losses in the air supply and to under- and overfeeding of the reactors, respectively. Additionally, a significant increase in the ambient temperature began at about the 160th day of operation and this may have severely impacted the performance of the reactors.

Some of these TOC fluctuations ultimately became rather extreme, as shown in Figure 7, resulting in failure of the 5-, 7.5-, and 10-day reactors despite up to six months of relatively stable performance. The variability in reactor behavior is clearly illustrated in Figure 8 which depicts the performance of the 20-day chemostat for more than one year of operation. There appears to be a six-month metastable period during which the effluent TOC averaged about 100 mg/l, followed by another three-month metastable period during which the effluent TOC averaged about 175 mg/l. The last three-month period of operation is marked by wide fluctuations in performance. These results suggest that, while dilution of the wastewater to 25% of full-strength overcomes the gross toxicity problem associated with the raw wastewater, treatment of the diluted wastewater by a chemostat system, such as an aerated lagoon, even at very long detention times, provides variable performance and is inherently an unstable system.

Accordingly, additional studies were carried out in reactors involving sludge recycle. Figure 9 shows the results of three reactors operated at a solids residence time of 20 days, with hydraulic retention times of 2, 5, and 10 days. Figure 10 shows performance data covering a twelve-month period for a second reactor with a 10-day hydraulic retention time and a 20-day sludge age. The extent of treatment, as measured by the effluent TOC for each reactor, appears to be approximately the same, with effluent TOCs averaging 200-225 mg/l (slightly higher and more variable for the 2-day HRT reactor). Comparing these effluent values to the influent TOC of the quarter-strength synthetic feed, the reactors provided an 80-83% reduction in TOC. The major "bumps" observed in the 10-day reactors, at 35 days (Figure 9) and 225 days (Figure 10) were caused by mechanical problems; the reactors were apparently able to overcome these operational malfunctions and return to a steady level of performance.

The conclusions reached from the data in Figures 9 and 10 are that a sludge age (SRT) of 20 days results in the same level of treatment,

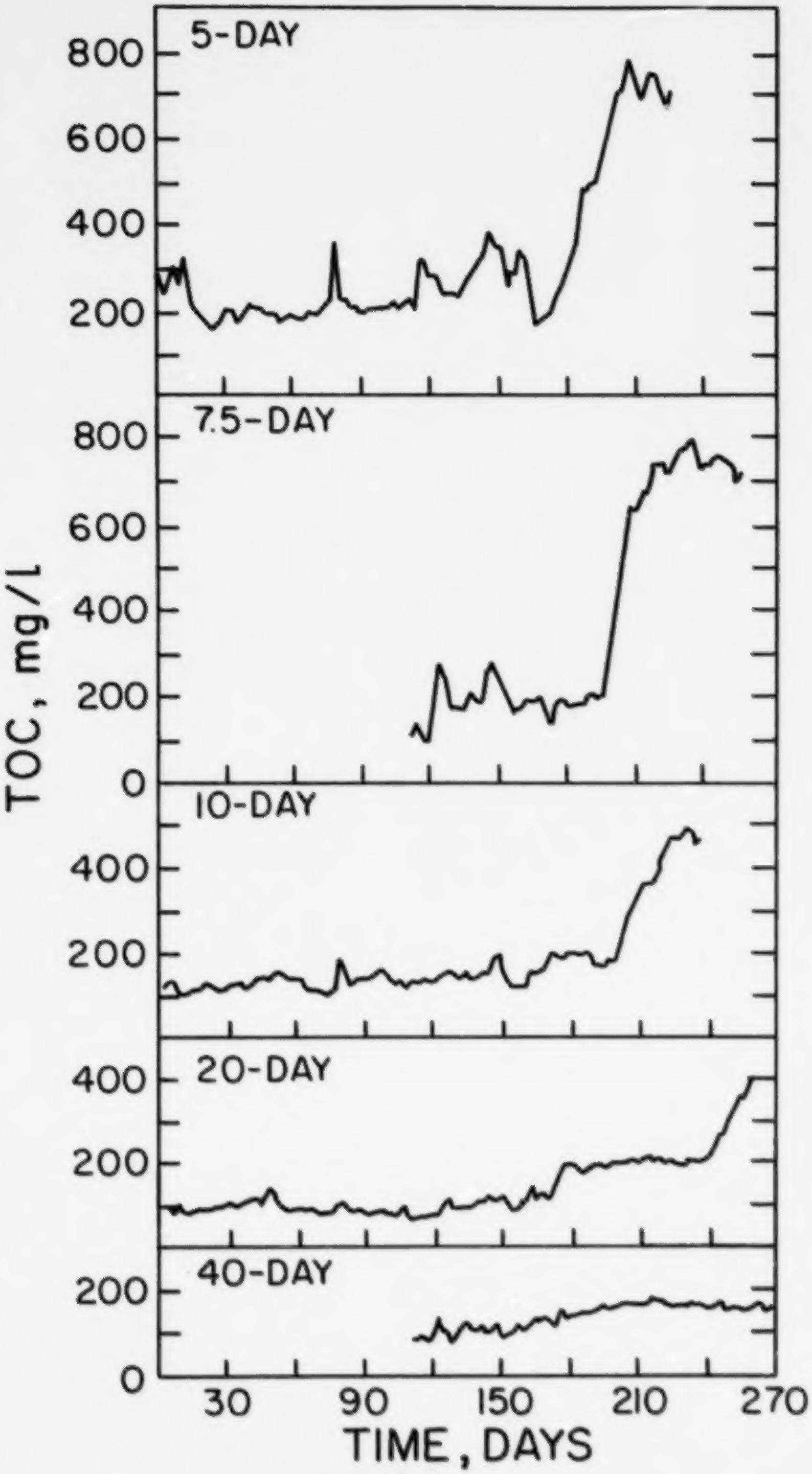

Figure 7. Summary of performance of chemostats treating 25% synthetic wastewater at different detention times.

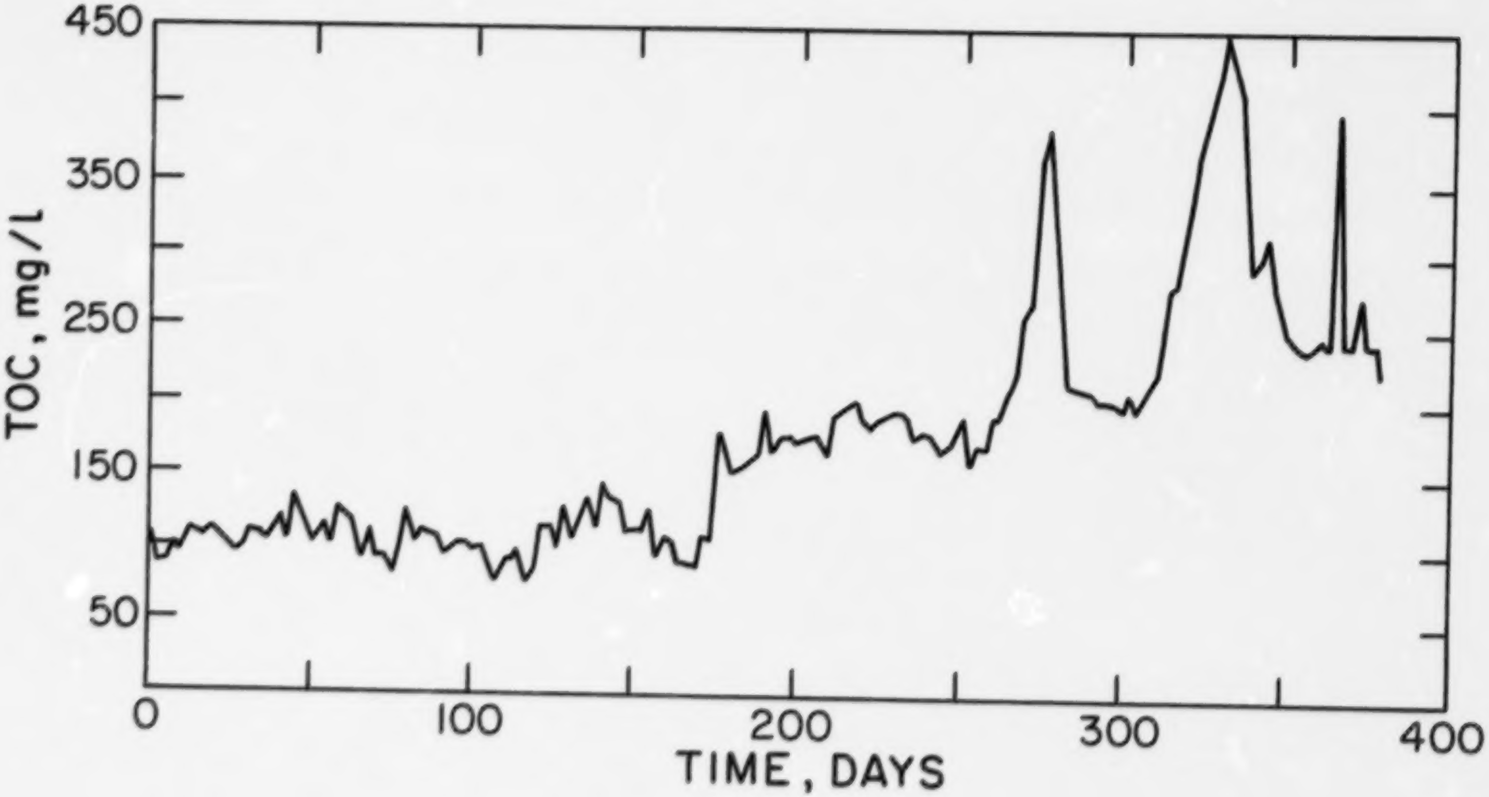

Figure 8. Long-term performance of 20-day chemostat treating 25% synthetic wastewater.

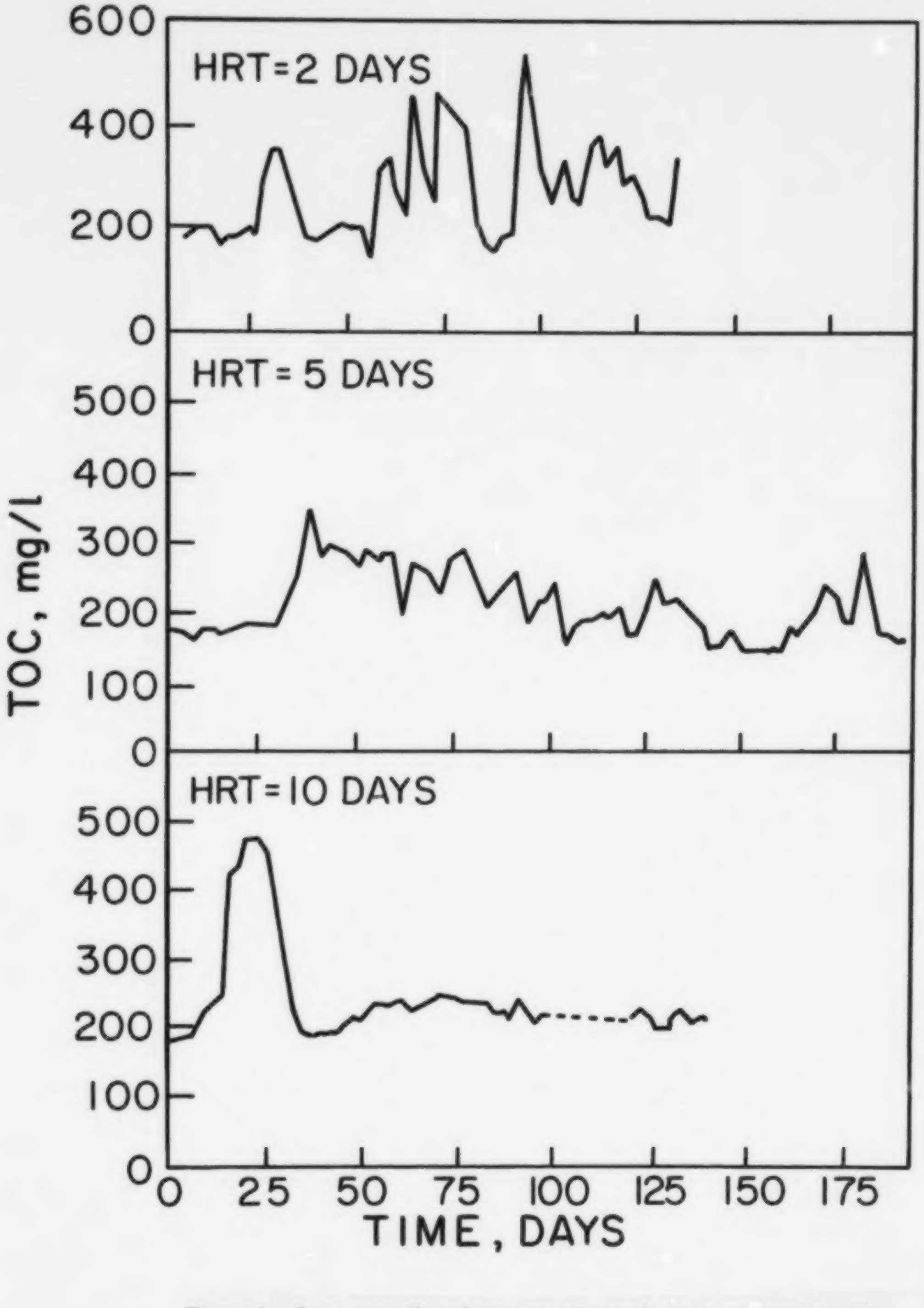

Figure 9. Summary of performance of recycle reactors treating 25% synthetic wastewater with 20-day sludge age and different hydraulic retention times.

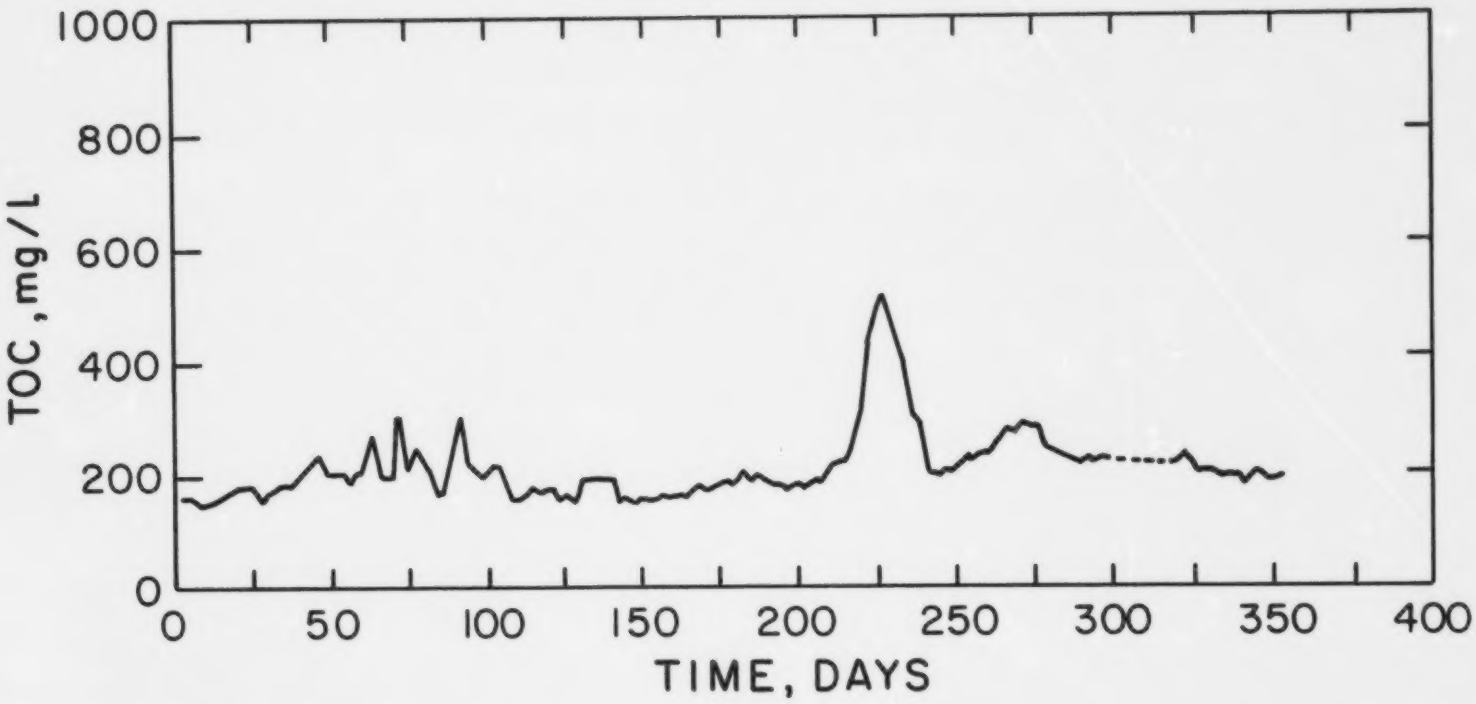

Figure 10. Long-term performance of recycle reactor with 20-day sludge age and 10-day hydraulic retention time.

regardless of the hydraulic residence time, but that control of the system is more difficult at lower HRTs, resulting in more variable performance. The long-term results shown in Figure 10 for the recycle system compared to the long-term results shown in Figure 8 for the 20-day chemostat demonstrates clearly the greater stability of the recycle system. Hence, more data on reactor performance under different conditions of operation (SRT and HRT) need to be developed using recycle systems in order to establish suitable design criteria for treating coal conversion wastewaters.

However, before this objective can be considered further, the question of toxicity of the wastewater constituents, associated with the failure of the reactors treating full-strength synthetic wastewater (see Figures 1 and 2), needs to be addressed. It should be noted that the full-strength reactors were started up using mixed liquor from the quarter-strength reactors, and gradually increasing the feed concentration from 25% to 100% strength. Accordingly, the microorganisms comprising the mixed liquor in these reactors should have been acclimatized to the wastewater constituents, at least at the lower dilution rate. Nevertheless, shortly after the wastewater feed reached full-strength, failure resulted, reflecting the accumulation of constituents in the reactor which were toxic to the microorganisms. As indicated previously, parallel results for the full-strength synthetic wastewater with the ammonia concentration reduced to 25% strength indicated that ammonia alone was not the causative agent in bringing about failure of the full-strength reactors.

In order to begin addressing the toxicity question in a systematic manner, a full-strength phenolics feed was formulated, the composition of which is shown in Table 2. This phenolics feed contains only the major phenolic constituents of the 28-component synthetic wastewater (compare Tables 1 and 2). The theoretical TOC of the phenolics feed is 3739 mg/l; hence, the seven constituents of the phenolics feed comprise 80.7% of the TOC in the 28-component synthetic wastewater (TOC = 4636 mg/l). It should be noted that the full-strength phenolics feed contains ammonia at a concentration 25% of that in the synthetic wastewater.

The full-strength phenolics wastewater was fed to a chemostat with a solids residence time of 20 days and to a recycle reactor with a solids residence time of 40 days and a hydraulic retention time of 20 days. The results are shown in Figure 11. Major fluctuations in the performance of each of the reactors are apparent. Most of these fluctuations appear to be related to documented mechanical problems associated with the operation of the feed system and the air supply. Again, the recycle system behaves in a more stable manner than the chemostat. Although some of the fluctuations were rather extreme, the reactors have recovered and have been treating the phenolic wastewater for more than four months, providing effluent TOC concentrations as low as 200-250 mg/l. Comparing this output to the TOC of the raw feed, this amounts to a 94-95% reduction in TOC. The concentration of total phenols in the treated water, as measured by wet chemical analysis on four occasions during this period, averaged 0.22 mg/l.

These results indicate that the full-strength phenolics wastewater, with a phenol concentration of 2000 mg/l, is biologically treatable. Hence, the toxicity problems associated with the 28-component full-strength

Table 2. CHARACTERISTICS OF PHENOLICS FEED

CHEMICAL	CONCENTRATION, mg/l
1. Phenol	2000
2. Resorcinol	1000
3. Catechol	1000
4. o-Cresol	400
5. p-Cresol	250
6. 3,4-Xylenol	250
7. 2,3-Xylenol	250
Theoretical TOC ===	3739 mg/l as C
NH_4Cl (250 mg/l as N)	955
$MgSO_4 \cdot 7H_2O$	22.5
$CaCl_2$	27.5
$NaHCO_3$	300
FeNaEDTA	0.34
PHOSPHATE BUFFER:	
KH_2PO_4	852
K_2HPO_4	2176
$Na_2HPO_4 \cdot 7H_2O$	3340

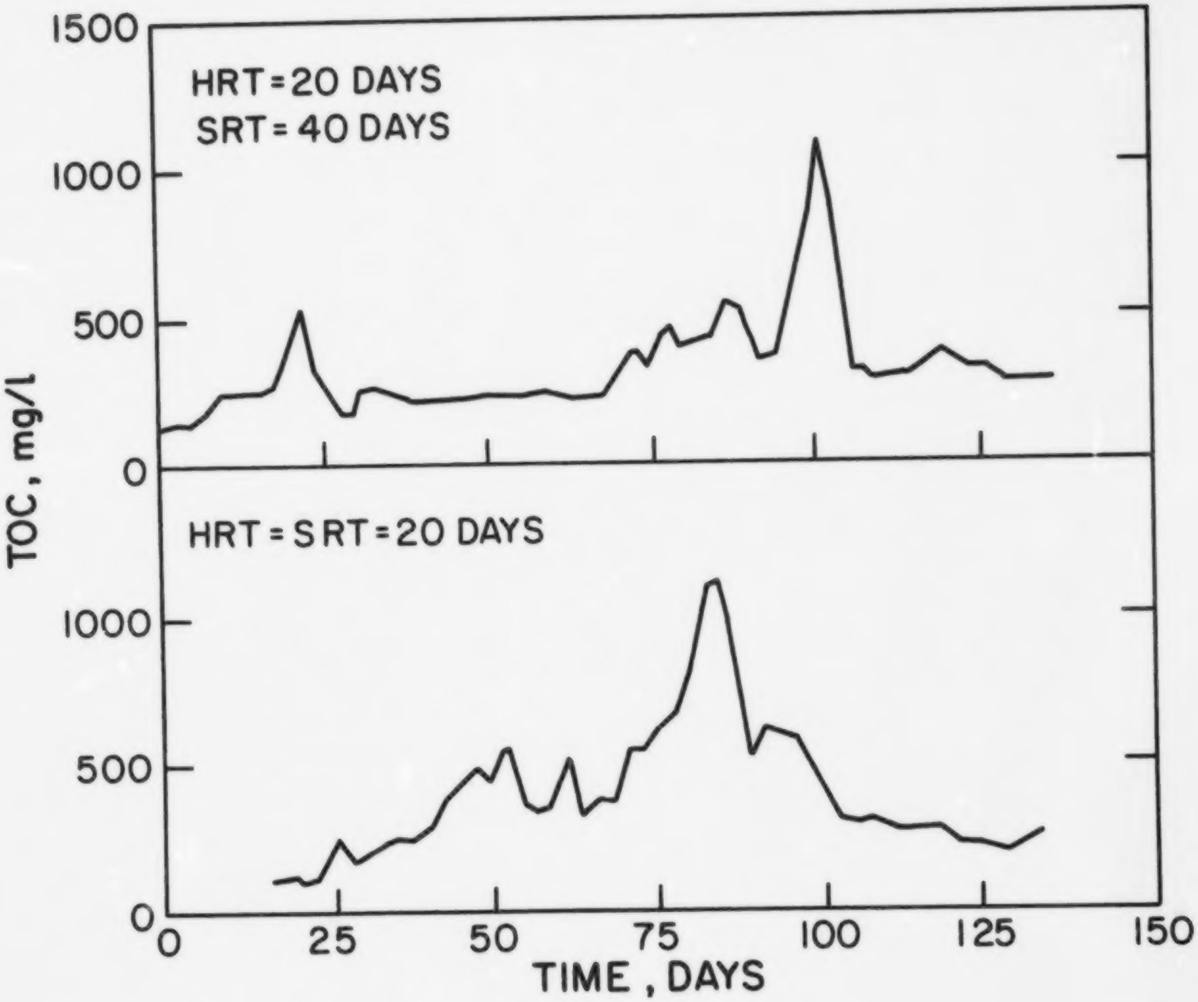

Figure 11. Biological treatability of full-strength phenolic wastewater.

synthetic wastewater must be due to one of the other minor constituents in the synthetic feed. Based upon parallel biodegradability studies of model compounds reported elsewhere,[6] leading candidates responsible for the toxicity problems include the pyridine and quinoline species, indole, acetophenone, and aniline. This toxicity question is being explored further by adding various of these additional constituents to the full-strength phenolics mixture, and feeding this "spiked" phenolic wastewaters to different biological reactors containing acclimatized mixed liquor from the reactors represented by Figure 11.

RESULTS OF DETAILED CHEMICAL ANALYSES AND BIOASSAYS OF REACTOR EFFLUENTS

Treated effluent from the chemostats treating the quarter-strength synthetic wastewater were collected at various times during the course of their operations and analyzed for residual BOD, COD, and phenols using standard methods of analysis.[7,8] Additionally, samples were subjected to specific organic analysis by high performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS). Aquatic bioassays involving algae, fish, and Daphnia, and mammalian cytotoxicity and Ames mutagenicity analyses were also conducted as a means of assessing the aquatic and health impacts, respectively, of the biologically-treated wastewater. Selected results from these detailed analyses are presented here. The results need to be interpreted with some care in view of the variability in reactor performance discussed above.

Wet Chemical Analyses

Table 3 shows the BOD, COD, and concentration of phenols in the effluent from the biological reactors for the days indicated. These values, compared to the measured influent concentrations, reflect the excellent degrees of treatment which were achieved, especially during the times when the reactors were performing in a reasonably stable manner. It should be noted that the concentration of phenols was measured using the 4-aminoantipyrine procedure[7,8] which responds only to certain of the phenolic constituents. It is apparent from Table 3 that BOD and phenols are virtually completely removed by the reactors having a solids retention time of at least 20 days, while COD and TOC removal does not improve to any great extent if the SRT is increased beyond 7.5 days. There appears to be approximately 100-160 mg/l of TOC with a COD of about 350-450 mg/l which is non-biodegradable in nature.

HPLC Analysis

Table 4 presents the results of HPLC analyses of the reactor effluents on the days indicated. Fresh samples of the reactor effluent were collected, filtered through 0.7 um glass fiber filters, and injected directly into the HPLC. Separation of the wastewater components in the samples was achieved using a 60-minute water/acetonitrile solvent gradient on a Waters uBondapak C_{18} analytical column. The eluted compounds were detected by both UV absorbance at 280 nm and fluorescence at 275 nm excitation and 310 nm emission wavelengths. Quantitation of the individual phenolic compounds shown in Table 4 was accomplished from the fluorescence measurements using effluent samples spiked with various quantities of the constituents in question. In some cases, the concentrations in the table

Table 3. SUMMARY OF WET CHEMICAL DATA ILLUSTRATING REACTOR PERFORMANCE. (All values in mg/l.)

	DAY	BOD	COD	PHENOLS
Raw Feed		1,780	2,830	575
5-day Reactor	126	112	670	-
	131	-	-	54
	133	126	670	-
	140	235	850	-
	147	485	1,160	-
	154	430	1,080	94
	161	360	825	-
	168	150	1,025	-
	169	-	-	33
	175	186	940	-
7.5-day Reactor	164	-	-	0.70
	168	10	570	-
	175	3	435	-
	185	6	445	-
	192	10	465	-
	194	-	-	1.16
10-day Reactor	126	5	480	-
	133	5	430	-
	140	5	460	-
	154	8	460	-
	161	9	470	0.62
	168	6	410	-
	175	6	460	-
	185	8	380	-
	192	6	465	-
	198	11	400	3.3
20-day Reactor	126	3	310	-
	133	2	370	0.43
	136	-	-	0.35
	140	4	355	-
	147	2	320	-
	150	-	-	0.35
	154	2	360	-
	157	-	-	0.29
	161	3	350	-
	168	2	400	-
	175	3	420	-
	185	2	415	-
	192	1	385	-

Table 3. (continued)

	196	-	-	0.19
	198	3	420	-
	203	-	-	-
	204	-	-	0.18
	210	3	450	-
	217	-	-	-
	218	-	-	0.22
	224	-	460	-
	226	3	-	-
	231	4	465	-
	233	-	-	0.25
40-day Reactor	193	-	340	-
	198	1	345	-
	205		-	0.11
	210	2	420	-
	212	-	-	0.18
	219	-	-	0.12
	224	-	430	-
	226	1	-	0.15
	231	-	-	-
	240	-	-	0.10
	252	1	375	-
	254	-	-	0.11
	259	1	-	-
	273	3	-	-
	282	-	-	0.09

Table 4. CONCENTRATIONS OF MAJOR PHENOLIC COMPOUNDS IN REACTOR EFFLUENTS (mg/1).

COMPONENT	RAW FEED	5-DAY REACTOR		7.5-DAY REACTOR	10-DAY REACTOR	20-DAY REACTOR	20-DAY REACTOR	40-DAY REACTOR
		DAY 163	DAY 175	DAY 188	DAY 176	DAY 176	DAY 185	DAY 303
PHENOL	500	0.9	0.6	<0.2	<0.4	<0.2	<0.1	<0.13
O-CRESOL	100							
P-CRESOL	62.5							
	162.5	22.2	30.2	0.2	0.8	<0.005	<0.02	0.036
3,4-XYLENOL	62.5							
2,3-XYLENOL	62.5							
3,5-XYLENOL	10							
	135	33.6	31.4	1.0	2.5	1.4	<0.01	0.007
2,3,5-TRIMETHYLPHENOL	12.5	9.0	7.0	0.6	1.3	<0.08	<0.02	<0.004
CATECHOL	250	<0.5	<0.5	<0.2	<0.5	<0.2	<0.1	<0.02
RESORCINOL	250	<0.5	<0.5	<0.2	<0.5	<0.2	<0.1	<0.02
TOC	1159	362	362	182	182	105	155	165

are shown as being less than a certain value; this value represents the detection limit of the fluorescence detector for that compound at the sensitivity used for that sample.

The HPLC results show that the removal of the phenolics increases with increased detention time and that phenol, resorcinol, and catechol are almost completely removed by the 5-day reactor. The cresols are completely removed (to concentrations less than 1 mg/l) within 7.5 to 10 days while a retention time of 20 days is required to reduce the concentrations of the xylenols and trimethylphenol below 1 mg/l. (It should be noted that the HPLC fluorescence procedure utilized is not capable of distinguishing among the various isomers of a given compound.) The HPLC results are in accordance with the phenol results reported in Table 3 in which the wet chemical aminoantipyrine procedure was employed.

The results in Table 4 are significant from the standpoint of reactor performance in that they show that the major phenolic constituents of the synthetic wastewater are removed by the biological reactors, and that the residual TOC in the effluent from the reactors is non-phenolic in nature. Parallel HPLC analysis using the UV detector indicates that a major portion of the residual TOC is comprised of highly polar compounds, e.g. aliphatic acids, presumably cellular metabolites arising from the biological degradation of the phenolics.

Acute Fish Toxicity

Samples of reactor effluent were collected continuously, over a 24-hour period, from the reactor overflow ports, and centrifuged and filtered to remove suspended solids. The samples were then frozen at -20°C. The low flow rates for some of the reactors, particularly those with long detention times, necessitated daily collection of the effluent over a relatively long time period until enough of the effluent could be collected to perform the bioassay. After a sufficient quantity of sample was available, the frozen samples were thawed and aliquots of the effluent were diluted with dechlorinated tap water to the desired concentration. Fathead minnows (Pimephales promelas) were used for the fish bioassay. Ten liters of each dilution were placed in a series of 5-gallon pickle jars, and 15 fish were added to each jar. Each test concentration was done in duplicate, so that a total of 30 fish were exposed to each concentration.

Figure 12 is a plot showing the percent mortality of the fish exposed for 96 hours to various dilutions of the raw feed and the various reactor effluents. The estimated 96-hour LC50 values, i.e. the lethal concentrations of the various wastewater samples causing death of 50% of the fish after 96 hours of exposure, are 1.1%, 6.6%, 33%, and 51%, respectively, for the quarter-strength synthetic feed and the 5-, 10-, and 20-day reactor effluent samples. As expected, toxicity decreases as the extent of the biological treatment increases.

Table 5 is a summary showing the characteristics of the wastewaters tested along with the LC50 values calculated from the results in Figure 12. The fact that the TOC concentration of the sample from the 10-day reactor is lower than that of the 20-day reactor is attributed to the composite nature of the samples. The samples were collected over a

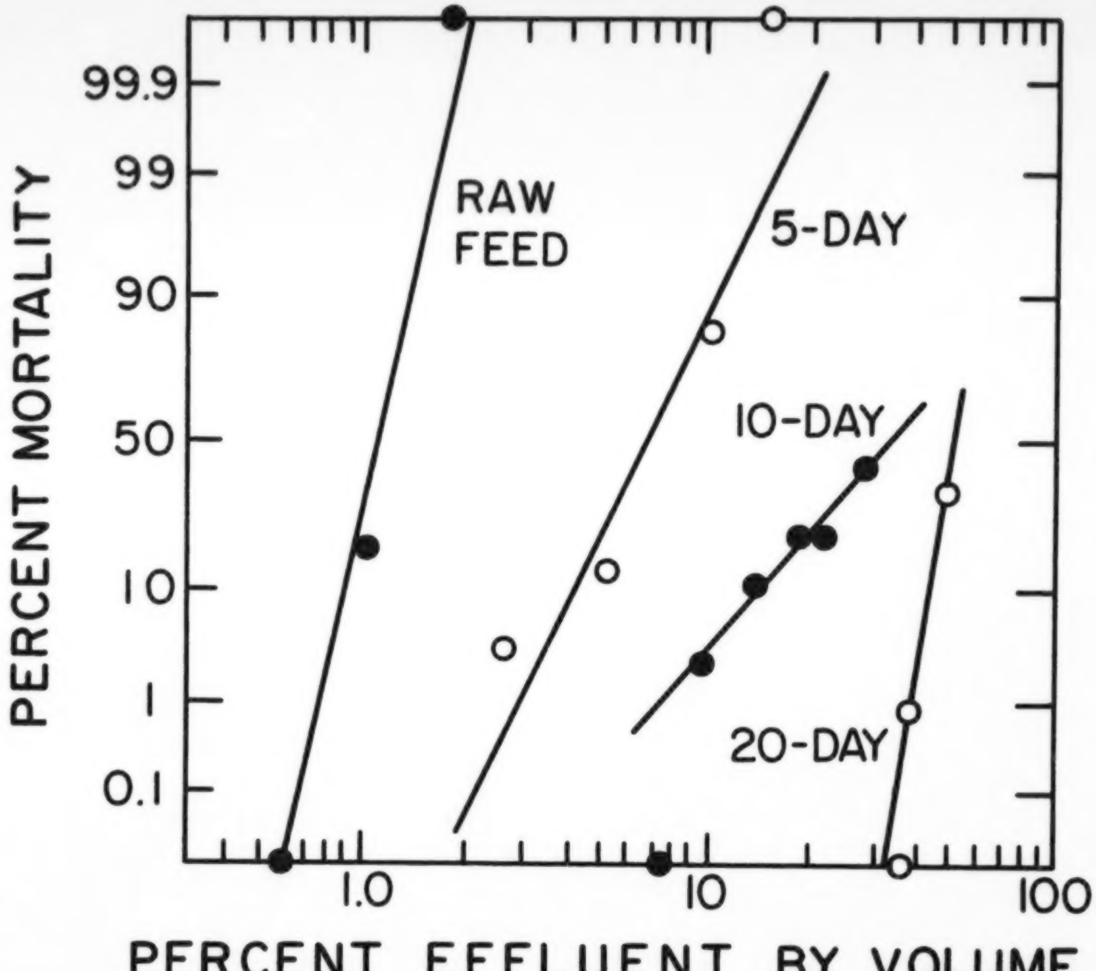

Figure 12. Acute toxicity of raw and treated synthetic wastewater to fathead minnows.

Table 5. RESULTS OF ACUTE TOXICITY TESTS USING FATHEAD MINNOWS

SAMPLE	TIME OF COLLECTION	TOC, mg/l	PHENOLS, mg/l	96-HOUR LC50, %	TOC AT LC50, mg/l	PHENOLS AT LC50, mg/l
RAW FEED	-----	1150	516	1.1	12.7	5.7
5-DAY REACTOR	Day 149-165	328	94	6.6	21.7	6.2
10-DAY REACTOR	Day 149-171	150	0.62	33	49.5	0.2
20-DAY REACTOR	Day 149-219	189	0.22	51	96.4	0.11

relatively long period of time, as noted, during which some degree of reactor instability was observed (see above discussion). The concentration of phenols, however, as measured by the wet chemical method, is in accordance with expectations, i.e. lower concentrations with increasing reactor detention times. The aquatic toxicity of the reactor effluent seems to be more closely related to the concentration of residual phenols and to the detention time of the reactors than to the residual TOC concentration; the LC50 for the sample from the 20-day reactor is 51% compared to 33% for the 10-day reactor sample despite the fact that the TOC of the latter is lower. Hence, the concentration of residual TOC, by itself, is not a satisfactory indicator of the aquatic toxicity of the treated wastewater. More information as to the composition of the various treated samples needs to be known.

Table 5 also shows the concentration of TOC and phenols at the percent dilution corresponding to the LC50s for each of the samples. It is apparent that the constituents comprising the residual TOC become correspondingly less toxic as the degree of treatment, as indicated by the detention time of the reactor, increases. Furthermore, a comparison of the last column in Table 5 with acute fish toxicity results for phenol alone (see Figure 13 where the 96-hour LC50 for phenol is shown to be 28 mg/l) indicates that the resulting toxicity of each of the composite samples, including the raw feed, cannot be attributed solely to phenol. The residual concentration of phenols at the LC50 dilution is, in each case, significantly less than the 28 mg/l LC50 for phenol. Hence, the aquatic toxicity of the treated samples must be due to constituents other than phenol, or to synergistic effects involving phenol and other constituents.

Mammalian Cytotoxicity

In order to evaluate the effectiveness of biological treatment in alleviating potential human health effects associated with coal conversion wastewaters, a clonal toxicity assay employing Chinese Hamster Ovary (CHO) cells[9] was used to compare the relative acute toxicities of the effluents from the biological reactors and the quarter-strength raw synthetic wastewaters. Effluent samples from the reactors were collected, centrifuged, aliquoted in small bottles, and stored at -80°C. Individual aliquots of the frozen samples were thawed immediately prior to use, filtered through a 0.2 um Nuclepore polycarbonate filter, and diluted with various amounts of deionized water and growth medium to obtain the desired concentrations.

Two hundred CHO cells were plated per tissue culture dish and allowed to incubate and attach for 3 hours in a normal cell growth medium. The medium was then removed and the appropriate dilution of the wastewater was added. After an exposure period of 20 hours, the test solution was removed. The cells were washed and reincubated in normal growth medium for 7 days. At the end of this incubation period, the colonies were fixed, stained, and counted.

Figure 14 is a plot of percent survival of the CHO cells for various dilutions of the different reactor effluents tested and the quarter-strength synthetic raw feed. The source of the different samples and the day of collection are shown in Table 6. Again, it should be noted

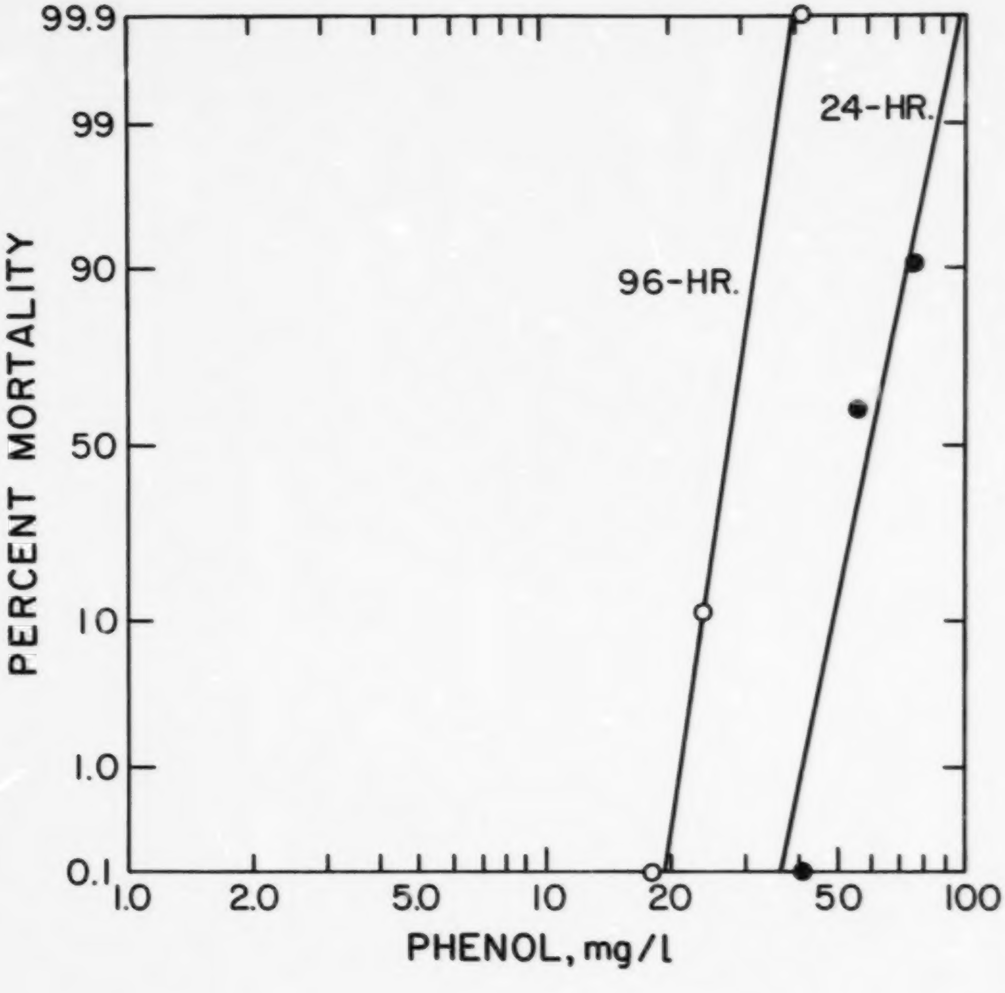

Figure 13. Acute toxicity of phenol to fathead minnows.

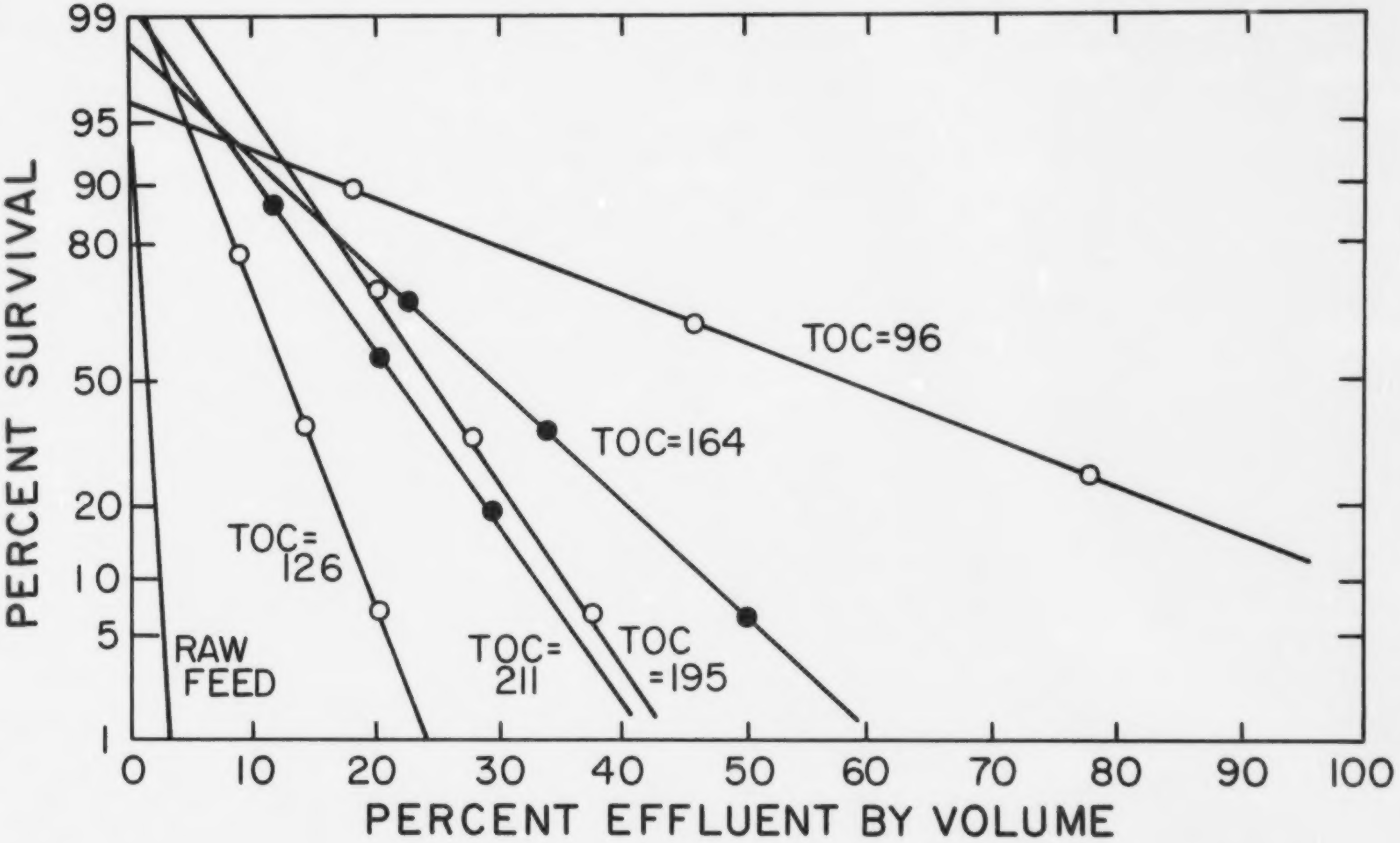

Figure 14. Cytotoxicity of raw and treated synthetic wastewater to Chinese hamster ovary cells.

Table 6. RESULTS OF CHO ACUTE MAMMALIAN CYTOTOXICITY TESTS

SAMPLE	DAY OF COLLECTION	TOC, mg/l	LC50, %..
Raw Feed	---	850	1.2
5-day Reactor	114	211	21.6
10-day Reactor	114	126	12.6
20-day Reactor	114	96	58.1
20-day Reactor	219	195	24.5
40-day Reactor	314	164	29.1

that the variability in reactor performance results in TOC values which are not entirely consistent with each other. For example, on two different dates, the effluent TOC concentrations from the 20-day reactor were 96 and 195 mg/l, resulting in very different cytotoxic responses. Figure 14 shows that, with the exception of the 10-day reactor and its corresponding TOC concentration of 126 mg/l, CHO toxicity decreases as effluent TOC decreases. The concentrations of each sample resulting in 50% lethality of the CHO cells, i.e. the LC50 values, are shown in Table 6. In contrast to the fish bioassay results, TOC appears to be a reasonably good indicator (with the exception of the 10-day reactor sample) of mammalian cytotoxicity. The anomalous behavior of the 10-day reactor cannot be explained.

Ames Mutagenicity

The Salmonella typhimurium mammalian-microsomal system was used to analyze the potential mutagenic activity of the raw and treated synthetic wastewater. All five Ames tester strains recommended for screening purposes were employed in this investigation. Two of the strains (TA100 and 1535) are capable of detecting mutagens which cause base-pair substitutions, while the other strains (TA98, 1537, and 1538) have the ability to detect frameshift mutagens. Standard experimental procedures for the plate incorporation assay, as outlined by Ames[10], were followed with one exception: due to the low concentrations of many of the chemicals present in the wastewater, 0.5-2.0 ml sample volumes were assayed instead of the standard 0.1 ml of sample per plate. The volume of the top agar overlay containing the various sample volumes was kept constant at 5.0 ml.

One-liter samples of reactor effluent were collected, centrifuged, aliquoted into smaller volumes, and stored at -80°C. Immediately prior to use, the wastewater was thawed and filtered through a 0.2 um Nuclepore polycarbonate filter. Each of the effluent samples as well as the raw feed was first examined to determine an acceptable range of sample volumes which would not be toxic to the bacterial strains and therefore would not preclude the mutagenicity testing.

The experimental scheme for determining the mutagenicity of the samples involved the assay of all the samples using one strain at a time, both with and without metabolic activation using an S-9 preparation of Arochlor 1254-induced rat liver microsomes. Positive control mutagens dissolved in dimethyl sulfoxide (DMSO), DMSO (solvent control), and an aqueous control were always assayed along with the wastewater samples. Mutagenicity studies were initiated with strain TA98 which has previously been reported to exhibit significantly increased mutation rates in the presence of the products of coal conversion processes.[11]

Table 7 demonstrates some of the results of the mutagenicity testing with strain TA98. A low level of direct-acting mutagenicity was found in the raw synthetic wastewater when assayed using 1.0 ml sample volumes per plate. Such activity was not observed in any of the reactor effluent samples, even when tested at 2.0 ml sample volumes. (The 5-, 10-, and 20-day reactor effluent samples were collected on Day 114 while the 40-day reactor effluent sample was taken on Day 314.)

Table 7. DIRECT-ACTING MUTAGENICITY OF RAW AND TREATED WASTEWATER SAMPLES WITH STRAIN TA98

	REVERTANTS/PLATE			MEAN	REVERSION RATIO*
Aqueous Control	31	26	32	30	(1)
1 ml Raw Feed	66	62	57	62	2.1
2 ml Reactor Effluents					
5-day	33	29	36	33	1.1
10-day	31	34	36	34	1.1
20-day	29	26	28	28	1 (0.93)
40-day	27	30	30	29	1 (0.98)
1 μg Daunomycin**	500	560	726	595	21.0
DMSO***	25	35	25	28	(1)

*Mean revertants on sample plate/mean revertants on control plate

**Used as positive control

***Solvent control for Daunomycin

Direct mutagenic activity was found in the raw wastewater with strains TA98 and TA1537, both of which detect frameshift mutagens. The mean reversion ratio with TA98 for five trials using the raw feed was 2.0 (see Table 8). Such a two-fold increase in the number of revertants over the control is the generally-accepted criterion for positive mutagenicity results. The mean reversion ratio with TA1537 for three trials (not shown) was 4.6. Results with TA1538 indicate that this strain was less sensitive to the frameshift mutagens in the raw wastewater than strains TA98 or 1537. There were no two-fold increases in reversion ratios found for any of the effluent samples, as demonstrated in Table 8 for the TA98 strain.

The synthetic wastewater also contains weak indirect mutagenic activity (not shown). Such activity requires the presence of a metabolic activation system (such as S-9 discussed above) for detection. When TA1535, a base-pair substitution detector, was used in the presence of S-9, the mean reversion ratio was 2.1 for three trials using the synthetic wastewater. No such increase was apparent for the effluent samples. Results were negative with the other commonly-used base-pair substitution strain, TA100, for the treated as well as the raw wastewater samples.

At this point, it can be concluded that biological treatment, even with a solids residence time of only 5 days, is capable of reducing the mutagenic activity associated with the raw synthetic wastewater to undetectable levels at the concentrations examined. These mutagenicity studies are continuing.

CONCLUSIONS

Based upon model studies using a synthetic coal conversion wastewater at 25% of full-strength and aerobic biological processes with and without solids recycle, coal conversion wastewaters appear to be biologically treatable. TOC, COD, and BOD removal increase with increasing solids residence time. Phenol is virtually completely removed with a sludge age of 5 days, while the cresols and xylenols require 7.5 to 10 days and 20 days, respectively, for removal to levels below 1 mg/l. Some difficulties were encountered in attaining stable reactor operation and steady-state performance was difficult to achieve. The reactors with sludge recycle demonstrated greater stability compared to the chemostats.

The full-strength synthetic coal conversion wastewater was found to be non-treatable biologically, presumably due to the presence of constituents at toxic levels in the full-strength sample. The toxicants do not appear to be any of the major phenolic components (i.e. phenol, resorcinol, catechol, cresols, xylenols). Studies are continuing to identify the constituent(s) responsible for the toxic behavior of the full-strength wastewater.

Bioassays of the raw and treated quarter-strength synthetic wastewater show that the acute toxicity of the raw wastewater to fish and to mammalian cells is markedly reduced as a result of biological treatment and that the reduction in toxicity increases with increasing sludge age. Additionally, at the concentrations tested, biological treatment reduces the mutagenic activity associated with the raw synthetic wastewater to undetectable levels..

Table 8. SUMMARY OF TA98 REVERSION RATIOS*

WITH RAW AND TREATED WASTEWATER SAMPLES

Without Metabolic Activation (S-9)

	RAW FEED	REACTOR EFFLUENTS (2.0 ml)			
TRIAL	(1.0 ml)	5-DAY	10-DAY	20-DAY	40-DAY
1	1.8	1.4	1.0	1.1	1.0
2	2.1	1.1	1.1	1.0	1.0
3	1.9	---	---	---	---
4	2.5	---	---	---	---
5	2.0	---	---	---	---
MEAN	2.0	1.3	1.1	1.0	1

*All ratios based on triplicate plates/sample.

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TREATMENT AND REUSE OF COAL CONVERSION WASTEWATERS

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This paper presents a synopsis of recent experimental activities to evaluate processing characteristics of coal conversion wastewaters. Treatment studies have been performed with high-BTU coal gasification process quench waters to assess enhanced removal of organic compounds via powdered activated carbon-activated sludge treatment, and to evaluate a coal gasification wastewater treatment train comprised of sequential processing by ammonia removal, biological oxidation, lime-soda softening, granular activated carbon adsorption, and reverse osmosis. In addition, treatment studies are in progress to evaluate solvent extraction of gasification process wastewater to recover phenolics and to reduce wastewater loading of priority organic pollutants. Biological oxidation of coal gasification wastewater has shown excellent removal efficiencies of major and trace organic contaminants at moderate loadings, addition of powdered activated carbon provides lower effluent COD and color. Gasification process wastewater treated through biological oxidation, lime-soda softening and activated carbon adsorption appears suitable for reuse as cooling tower make-up water. Solvent extraction is an effective means to reduce organic loadings to downstream processing units. In addition, preliminary results have shown that solvent extraction removes chromatographable organic contaminants to low levels.

TREATMENT AND REUSE OF COAL CONVERSION WASTEWATERS

INTRODUCTION

Experiments have been performed at Carnegie-Mellon University to characterize coal gasification process wastewaters, to evaluate basic wastewater treatment properties, and to assess wastewater management strategies. The purpose of this paper is to review recent experimental activities in these areas, and to indicate directions for future research.

COAL GASIFICATION WASTEWATER MANAGEMENT

Figure 1 presents a general schematic representation of water streams important in coal gasification process water balances. Major streams include those associated with the boiler and cooling tower systems, process condensates, treatment blowdowns, and slurry/sludge waters. Process influent water streams generally include: water for coal slurry feed, water for direct contact gas cooling or quenching, and water for removal and/or quenching of char, ash, or slag. Process steam requirements include steam to gasifier and make-up steam to CO shift reactor. Process effluents are categorized as slag or ash quench water, raw product gas quench condensate, CO shift condensate, acid gas removal condensate and methanation condensate. The nature and quantities of these process water and effluent streams are highly process specific. The disposition of these streams for particular high BTU coal gasification processes is discussed in Luthy, et al., 1980[1], for the CO_2-Acceptor, Bi-Gas, Hygas, Synthane, and Lurgi processes.

Specific process water treatment and distributional configurations are also strongly dependent on the particular gasification process being considered. Thus various water management schemes exist for different gasification processes. Some aspects of these schemes are well understood and have become generally accepted as necessary in achieving a process water balance. For example, raw makeup water is typically softened and serves as process water, as cooling water, and as supply to the boiler feed water treatment system. In contrast some aspects of high BTU coal gasification process water balance are unique to this industry. This is especially true with respect to treatment and reuse of heavily contaminated phenolic wastewaters. In this case little previous experience is available to detail issues associated with treatment and reuse of these wastewaters; consequently, current research interest is focused on evaluation of specific treatment characteristics for purposes of engineering design and environmental assessment. There is also much interest in evaluating wastewater treatment characteristics in order to achieve a product water of suitable quality for reuse in the gasification process.

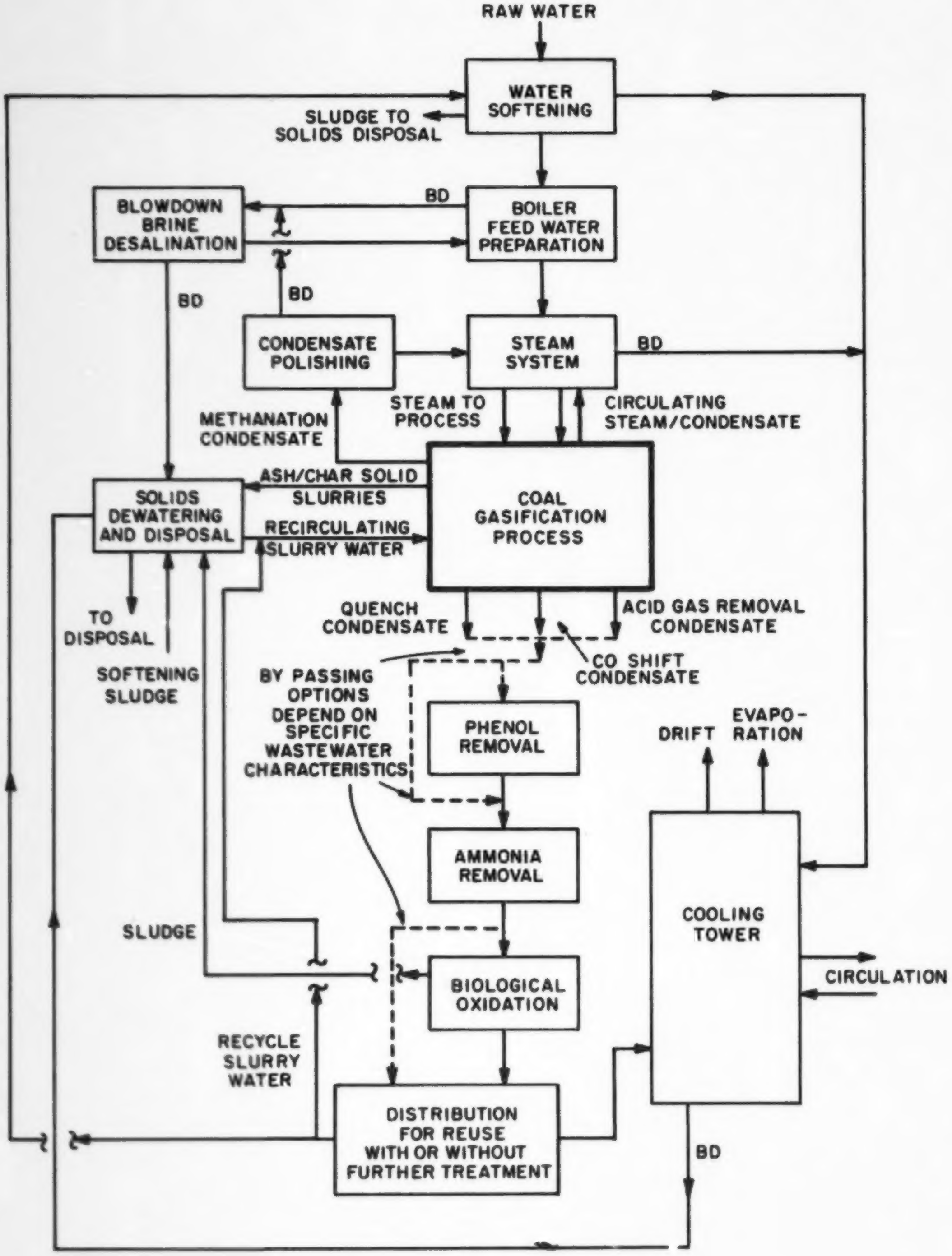
RAW WATER
WATER SOFTENING
SLUDGE TO SOLIDS DISPOSAL
BLOWDOWN BRINE DESALINATION
BD
BOILER FEED WATER PREPARATION
BD
BD
CONDENSATE POLISHING
STEAM SYSTEM
BD
METHANATION CONDENSATE
STEAM TO PROCESS
CIRCULATING STEAM/CONDENSATE
SOLIDS DEWATERING AND DISPOSAL
ASH/CHAR SOLID SLURRIES
RECIRCULATING SLURRY WATER
COAL GASIFICATION PROCESS
TO DISPOSAL
SOFTENING SLUDGE
QUENCH CONDENSATE
ACID GAS REMOVAL CONDENSATE
CO SHIFT CONDENSATE
BY PASSING OPTIONS DEPEND ON SPECIFIC WASTEWATER CHARACTERISTICS
PHENOL REMOVAL
DRIFT
EVAPO-RATION
AMMONIA REMOVAL
COOLING TOWER
SLUDGE
BIOLOGICAL OXIDATION
CIRCULATION
RECYCLE SLURRY WATER
DISTRIBUTION FOR REUSE WITH OR WITHOUT FURTHER TREATMENT
BD

Figure 1. Major water streams in a coal gasification process water balance.

Considerations Regarding Water Reuse

Medium and high-BTU coal gasification processes are net consumers of water. The ability to achieve complete water reuse may have a significant impact on the feasibility of a commercial-scale facility, especially for semi-arid western regions and for eastern sites not contiguous or adjacent to large rivers. A general design assumption should hold that all major wastewater streams be considered for reuse, including high organically contaminated streams and saline brines. Dirty water should be cleaned only for reuse and not for discharge to a receiving water; any water suitable for discharge is acceptable for reuse. Returning water to a source is not economic when water must be cleaned to satisfy stringent environmental regulations. Furthermore, treatment for reuse is likely to require less severe processing than treatment for discharge.

Various water management schemes exist for a given gasification process. These depend on the exact nature of the particular waters and on the quality constraints for which waters will be reused. Though specific processes may differ in water management configurations, it is apparent that the cooling tower is the most likely target for wastewater reuse. Treatment for reduction of high ammonia and organic loadings is necessary, while some extent of demineralization and removal of residual organic contaminants will be necessary to achieve a water within quality constraints governing cooling tower makeup. Minimum quality constraints governing acceptable levels of organic contamination in cooling tower make-up are not clearly understood and must be evaluated. Also the fate of toxic hazardous wastewater contaminants during wastewater treatment and during cooling tower operation must be assessed. These factors will ultimately determine the most appropriate treatment scheme to achieve water reuse in a cooling tower.

WASTEWATER CHARACTERISTICS AND SCALABILITY

High-BTU coal gasification processes may be divided into two general classifications with respect to levels of organic contamination in process condensates: 1) those processes which produce little or no phenolics, oils, and tars, and 2) those processes which produce substantial quantities of these materials. Among those processes which produce organic contaminants a further division may be made between those which are significant producers of tars and heavy oils. General data for comparison of coal refinery condensates are presented in Luthy, 1979.[2]

The production of organic contaminants during coal gasification is related to gasifier physical configuration and operating conditions. Processes tending to show little or no organic contamination may be either entrained flow or fluidized bed gasifiers that operate at temperatures greater than approximately 1050°C (1900°F) and produce ash as slag or agglomerates. Examples of such processes are Bi-Gas, Combustion Engineering, Koppers-Totzek, U-Gas, and Westinghouse. Gasifiers having high coal devolatilization temperatures, such as the CO_2-Acceptor process at 830°C (1500°F), also produce a cleaner product gas which in turn yields condensates free of organic contamination (Fillo, 1979[3]). Other important gasifier operating variables which relate to production of organics are gas residence time, coal particle size and heat-up rate, and the extent of gas-solids mixing (Nakles, et al., 1975[4]). Examples of gasification processes which produce effluents with organic contamination are Hygas, Synthane, slagging fixed-bed, Lurgi, and Wellman-Galusha.

It should be recognized that published information on coal gasification process wastewater characterization necessisarily reflects a difference in process scales and use of various coals. Since much of the available data are for analysis of condensates from process development units or pilot plants, it should be expected that any changes anticipated between pilot plant and commercial scale gasifier operating conditions may have significant effects on gasifier effluent production, especially with respect to organic contamination. Thus, scalability of pilot plant data is a major issue in evaluating coal conversion pilot plant effluent composition and distributional trends. Factors to consider may include coal type and pretreatment, coal-to-steam ratio, gasifier geometry and operating parameters, and raw product gas quench system design and operation.

Wastewater treatment experiments performed at Carnegie-Mellon University have utilized process quench waters from the Hygas and slagging fixed-bed coal gasification pilot plants. While these process condensates may not be representative in a quantititative sense of wastewaters which would be expected in a demonstration or commercial scale process, it is anticipated that the majority of organic and inorganic species observed in these effluents may be expected to exist in a commercial facility, though relationships between mass emissions and concentrations may be somewhat different. In as much as the scope of the investigations were to obtain basic information on biological and physico-chemical treatability characteristics of gasification effluents, the pilot plant wastewater samples were envisioned as providing a reasonable matrix of representative contaminants which may be expected in presently conceived commercial facilities.

TREATMENT STUDIES WITH COAL GASIFICATION CONDENSATES

There exists only a limited number of published studies on treatment of organically contaminated coal gasification process wastewaters, especially for the new generation of gasification processes under development. Most of those studies have focused on physico-chemical treatment for reduction of tars, oils, and ammonia prior to biological oxidation, and on basic biological oxidation characteristics of these wastewaters. These data are largely based on experience gained from laboratory bench-scale experimentation.

Experimental biological oxidation studies have been reported for Lurgi coal gasification process effluent (Cooke and Graham, 1965[5]), Synthane (Johnson, et al., 1977[6]; Neufeld, et al., 1978[7]; and Drummond, et al., 1979[8]) and Morgantown Energy Technology Center (METC) pilot coal gasification wastewaters (Sack, 1979[9]), and H-Coal pilot coal liquefaction effluent (Reap, et al., 1977[10]). In addition, biological oxidation studies have been performed with pilot coal gasification process effluents obtained from the Hygas pilot plant operated by the Institute of Gas Technology in Chicago, Illinois (Luthy and Tallon, 1980[11]) and the slagging fixed-bed pilot plant operated by the Grand Forks Energy Technology Center (GFETC) in Grand Forks, North Dakota (Luthy, et al., 1980[12]).

A discussion of performance data and biological oxidation kinetic values for treatment of coal conversion wastewaters is presented in Luthy (1979[2]). A general conclusion from these investigations is that wastewaters processed for removal of ammonia by steam stripping followed by activated sludge treatment for removal of degradable organic matter will show high removal efficiencies for BOD, COD, phenolics and thiocyanate. Nitrification has been demonstrated in several investigations. However, because of the nature of coal gasification process condensates, activated sludge treated wastewater will contain relatively high concentrations of residual organic material. This material is associated with effluent COD and color and is characteristic of oxidation of complex phenolic wastes.

REMOVAL OF TRACE ORGANIC CONTAMINANTS

Less information is available on the trace organic composition of coal gasification wastewaters and removal efficiencies for these compounds during treatment. Singer, et al. (1978) summarizes organic characterization data for coal conversion effluents. Information on removal efficiencies for specific organic compounds from synthetic coal conversion wastewater mixtures is presented in Singer, et al. (1978[13], 1979[14]).

Stamoudis and Luthy (1980[15]) provide results of screening gas chromatography/mass spectrometry analysis of Hygas and GFETC pilot plant wastewater to determine removal efficiencies during biological oxidation. In these investigations wastewater was pretreated by lime addition and air stripping to reduce excess alkalinity and ammonia prior to biological oxidation. The biological reactors were complete-mix, single-stage air activated sludge reactors, with GFETC wastewater being treated at 33% strength and Hygas condensate at 100% strength. General operating parameters and performance characteristics for the biological reactors employed for evaluation of removal efficiencies of organic constituents are summarized in Stamoudis and Luthy (1980[15]). Samples of reacter influent and effluent were prepared for GC/MS analysis by extraction with methylene chloride using generally accepted techniques into acid, base and neutral fractions.

It was found that approximately 99% of influent extractable and chromatographable organic material, on a mass basis, was derivatives of phenol and represented in the acid fraction of the influent samples. Activated sludge processing removed most of the organic constituents, with compounds of the acidic fractions being removed almost completely. High removal efficiencies were also observed for compounds in the basic fraction, with the exception of certain alkylated pyridines. The extent of removal of compounds in the neutral fractions was dependent on chemical structure. Aromatic hydrocarbons containing aliphatic substitutions and certain polynuclear aromatic compounds were only partially removed. A general broad conclusion from this study was biological oxidation provides good to excellent removal for most compounds present in the coal gasification process wastewater.

Followup studies were conducted with GFETC slagging fixed-bed pilot plant wastewater pretreated in the same fashion as above in order to compare removal of organic contaminants by activated sludge and powdered activated carbon (PAC)-activated sludge treatment. Details of the experimental procedures and results are presented in Luthy, et al. (1980[1]).

A high suface area PAC (Amoco PX-21) was selected for use in this study on the basis of results from wastewater batch adsorption isotherm testing. PAC-activated sludge treatment was evaluated at sludge ages of twenty and forty days with PAC mixed liquor equilibrium concentrations of 0, 500, 1500, and 5000 mg/l. The reactors were operated for an appropriate balance period to achieve steady state operation.

Activated sludge treatment with no addition of PAC showed excellent removal of phenolics and BOD. Phenolics were reduced to less than 1 mg/l from influent values of 1300-1500 mg/l; BOD was reduced to about 30 mg/l from influent concentration of 3600-3800 mg/l. COD removal efficiencies were 85% and 88% at removal rates of 0.37 and 0.24 mg COD removes/mg MLVSS-day at sludge ages of twenty and forty days, respectively.

PAC-activated sludge treatment gave significantly lower effluent COD and color with increasing equilibrium carbon concentrations. In addition, somewhat lower effluent concentrations of BOD, phenolics, ammonia, organic-nitrogen, and thiocyanate were achieved by PAC-activated sludge treatment compared to activated sludge treatment. PAC-activated sludge treatment reduced foaming problems and gave a sludge with good settling properties. Effluent characteristics were not significantly different for PAC-activated sludge treatment at a sludge age of twenty and forty days. In general, PAC-activated sludge treatment in this study gave as good or better effluent characteristics than previously reported results with other industrial wastes. A highly nitrified effluent was produced by PAC-activated sludge treatment at a sludge age of forty days. This effluent appears suitable for reuse as cooling tower make-up water with respect to macro-organic contaminants.

Samples of biological reactor effluent with sludge age of forty days and mixed liquor PAC concentrations of 0, 500, 1500, and 5000 mg/l were screened for base and neutral fraction organic compounds. Base and neutral fraction capillary column chromatograms of all four reactors were very similar. Characterization of sixteen compounds, representing some of those which were found not to be completely removed in the previous GC/MS study with slagging fixed-bed wastewater, gave similar GC flame ionization detector responses in effluent samples for all four reactors with concentration levels of these compounds in the range of several mg/l. These results confirmed that biological oxidation of coal gasification wastewaters removes organic contaminants to low levels, however PAC-activated sludge treatment does not necessarily provide significantly lower effluent concentrations of certain trace organic compounds under conditions in which the biological oxidation process has been optimized. The PAC results can be explained in part on competition adsorption between very low concentration of base and neutral fraction compounds and very high concentration of oxidized and/or polymeric substances resulting from biological treatment of phenolic wastes. These later substances are similar to humic materials and are associated with residual effluent COD and color. These substances are removed significantly by PAC-activated sludge treatment, and they likely compete with trace organic contaminants for adsorption on the powdered activated carbon.

EVALUATION OF A COAL GASIFICATION WASTEWATER TREATMENT TRAIN

A sample of Hygas pilot plant Run 79 coal gasification quench condensate has been processed through sequential wastewater treatment unit operations to evaluate treatment technology to achieve wastewater reuse. The unit operations investigated in this study are shown in Figure 2 and include: ammonia removal, biological oxidation, lime-soda softening, activated carbon adsorption, and reverse osmosis.

The raw wastewater contained approximately 0.86 meqv/l of alkalinity and 0.94 meqv/l of ammonia at pH of 7.7. These results plus batch steam stripping tests showed that approximately 97% of the ammonia can be liberated in one unit operation without chemical addition. Removal of the remaining fraction of ammonia will require addition of lime or caustic. If lime is used, this will result in a significant increase in wastewater hardness (>1000 mg/l as $CaCO_3$). In this study, steam stripping was simulated by liming to precipitate alkalinity and air stripping to remove ammonia. The residual hardness in stripped wastewater was in the same range regardless if free- and fixed-leg steam stripping or liming and air stripping were used for ammonia removal.

Biological oxidation at a COD removal rate of 0.16 mg COD removed/mg MLVSS-day gave 90% reduction in COD from an influent value of 6900 mg/l, and 99% reduction in BOD from an influent value of 3500 mg/l. There was also 96% removal of thiocyanate and reduction of phenolics to 0.7 mg/l. Biologically treated wastewater contained about 30 mg/l BOD, 700 mg/l COD, and 1200 mg/l hardness (as $CaCO_3$). It was judged that if biologically treated wastewater were to be used as make-up to a cooling tower, that the COD was sufficiently high to promote potentially significant biological activity, and that calcium and sulfate levels could lead to scaling and fouling problems. Therefore, removal of calcium hardness was evaluated by lime-soda softening,

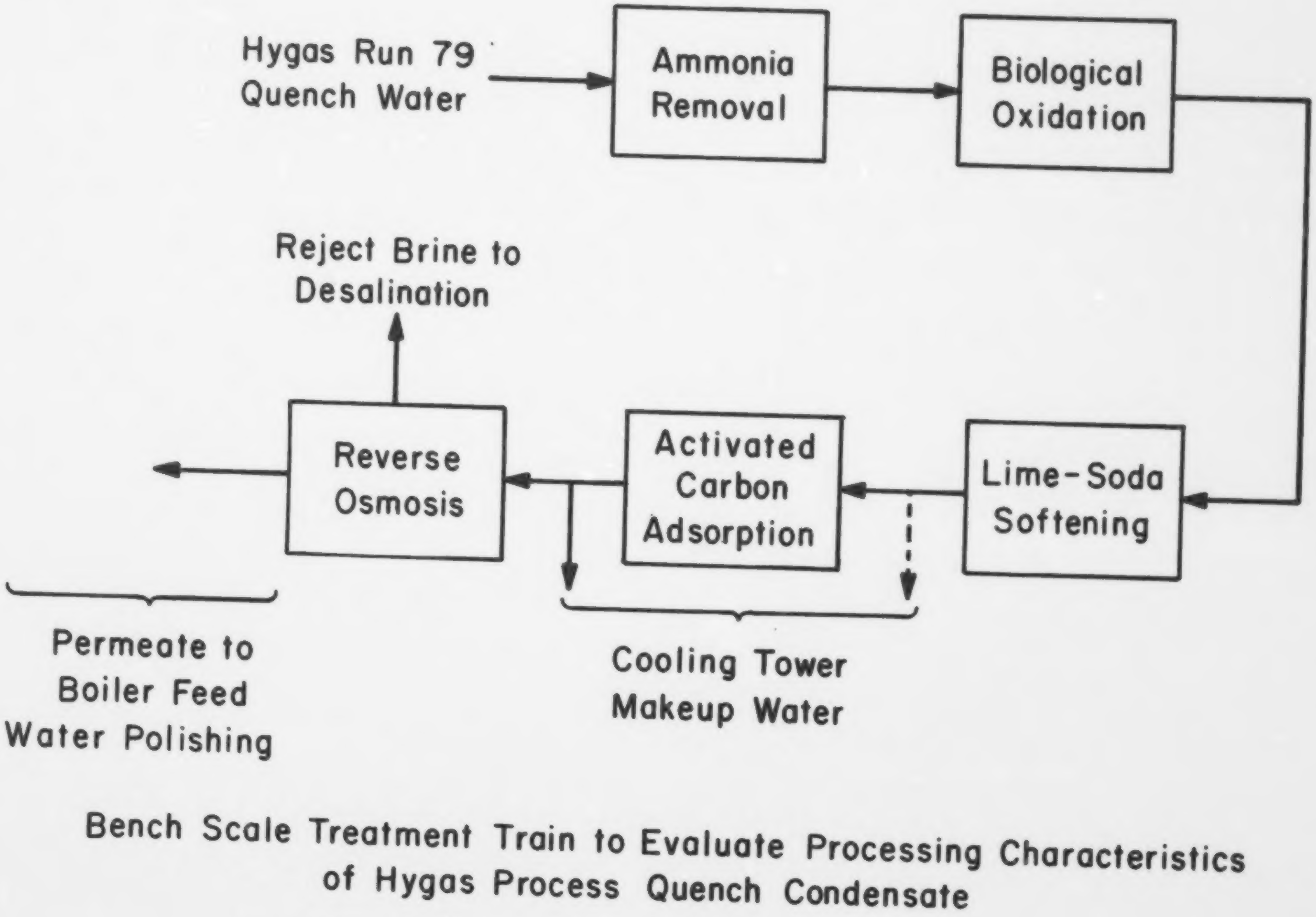
Hygas Run 79
Quench Water
Ammonia
Removal
Biological
Oxidation
Lime-Soda
Softening
Activated
Carbon
Adsorption
Reverse
Osmosis
Reject Brine to
Desalination
Permeate to
Boiler Feed
Water Polishing
Cooling Tower
Makeup Water
Bench Scale Treatment Train to Evaluate Processing Characteristics
of Hygas Process Quench Condensate

Figure 2. Bench Scale Treatment Train to Evaluate Processing Characteristics of Hygas Process Quench Condensate.

and removal of COD was assessed by granular activated carbon treatment of softened wastewater.

Most of the calcium hardness in biological reactor effluent existed as non-carbonate hardness owing to the consumption of alkalinity during biological oxidation. Thus, lime-soda softening required proportionally more soda than lime. This resulted in the replacement of residual wastewater equivalents of hardness by equivalents of sodium. Lime-soda softening reduced wastewater hardness to practical limits (30-40 mg/l as $CaCO_3$). These tests also indicated that flocculation and/or filtration would be necessary to clarify sludge formed by the softening operation. Granular activated carbon adsorption column testing of softened biological effluent was conducted at pH of 7, a contact time of seventeen minutes, and a loading of about 1.2 gpm/ft^2. These tests showed that approximately 80% of COD and 95% of residual color could be removed by carbon adsorption.

Hygas wastewater processed by ammonia removal, biological oxidation, lime-soda softening, and activated carbon adsorption was judged to be of sufficient quality for reuse as cooling tower make-up water. At this time it is not possible to predict the degree of cooling tower biological activity which may be induced by residual COD of about 100 mg/l in carbon treated effluent, although it is suspected that a biocidal program could control this problem.

Reverse osmosis experiments were conducted with granular activated carbon treated wastewater. Reverse osmosis treatment with a hollow fiber polyamide membrane produced a clear colorless product, with a TDS level comparable to tap water. Low levels of organic contaminants (COD = 20 mg/l) did permeate the membrane. It is believe that these compounds were low molecular weight, and that they permeated the membrane owing to preferential sorption at the membrane-solution interface. Product water from reverse osmosis treatment is suitable for reuse as make-up to a boiler feed water polishing facility.

Reverse osmosis membrane fouling was not observed in this study under operation at 75 percent conversion. Addition of a polyphosphate inhibitor is thought to have been at least partially responsible for this. A decline in membrane flux did occur, but this was primarily a result of membrane compaction. Comparison of polyamide and cellulose triacetate hollow fiber membranes showed that the polyamide membrane provided a higher quality product water while the cellulose triacetate membrane provided higher flux rates.

This investigation showed that a possible treatment scheme for reuse of phenolic coal gasification effluents may include provisions for ammonia stripping, biological oxidation, softening, and activated carbon adsorption. These unit processes will provide a water with sufficient quality for reuse as cooling tower make-up water. Further study is required to assess the possibility of excessive biological activity and/or emissions of trace compounds to the environment as a result of wastewater reuse in cooling towers. Resolution of this problem may depend on large pilot cooling tower studies and on operational experience gathered at demonstration plants.

Reverse osmosis appears to be an attractive technique to remove wastewater dissolved solids. If reverse osmosis is employed in treatment system design, the resulting product water will be of sufficient quality to be used as a boiler feedwater source. However, further study needs to be undertaken to determine the extent of membrane fouling that could possibly occur under long term steady state operation. It is probably best to evaluate reverse osmosis treatment units at the pilot scale once demonstration plants have been built.

EVALUATION OF A PROPOSED TREATMENT TRAIN FOR A DEMONSTRATION PLANT

Figure 3 shows a simplified schematic of a proposed wastewater treatment system for a slagging Lurgi process to gasify Illinois No. 6 bituminous coal (Continental Oil Company, 1979[16]). Wastewater treatment at this proposed facility handles streams discharging to an oily water sewer, Rectisol process blowdown, solvent extracted wastewater from ammonia recovery, and sanitary wastewater. As shown in Figure 3, the treatment train for wastewater from ammonia recovery passes to an equalization basin and then to a dissolved air flotation unit. Wastewater is then treated biologically in an extended aeration basin of three days hydraulic detention time. Effluent from the biological reactors is clarified, processed through polishing filters, and then pumped through granular activated carbon columns for removal of residual organics. Wastewater from the activated carbon unit is pumped to the utilities cooling tower.

The utilities cooling tower supplies cooling water to equipment having ordinary or carbon steel metallurgy. Makeup to the utilities cooling tower is obtained from various sources of which blowdown from the process cooling tower comprises the largest portion of the total. Makeup from wastewater treatment comprises about 17% of the total demand. The plant is designed for zero discharge of wastewater. The key units for this are multi-stage and Carver-Greenfield evaporators. The multi-stage evaporator concentrates an approximate one percent feed to an approximate 30 weight percent salt solution. The condensate is recovered in the utility cooling tower and the salt solution is concentrated to an approximate 60 weight percent aqueous slurry. The concentrated salt mixture is chemically fixed and trucked to a landfill. Continental Oil Company recommended that semi-commercial evaporators be constructed and evaluated prior to constructing large units because no commercial experience exists with wastewater from a gasification facility, and there may be problems with scaling and foaming.

Figure 4 shows a schematic representation of experiments in progress to evaluate essential features of a wastewater treatment train of the

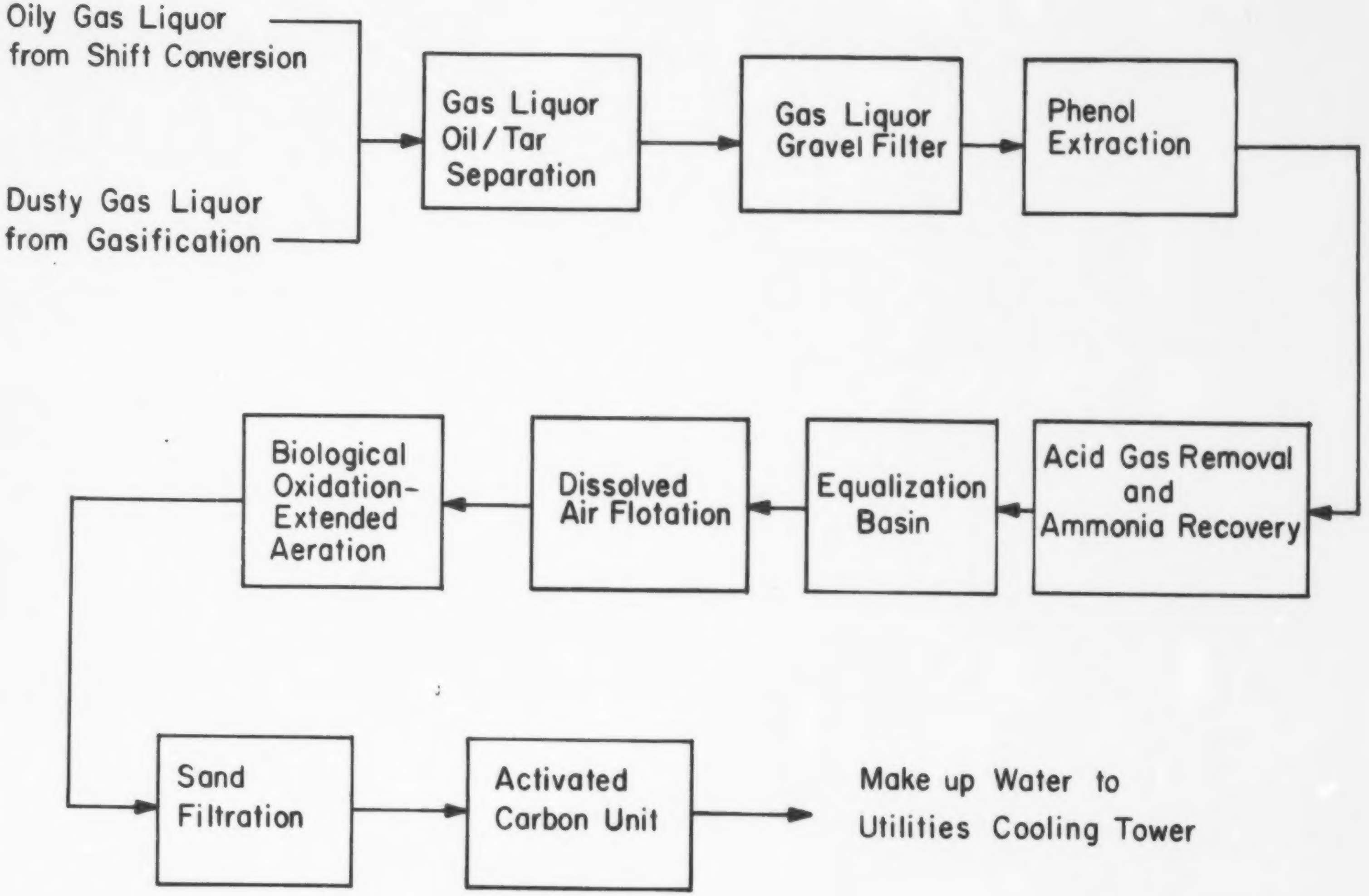
Oily Gas Liquor from Shift Conversion
Dusty Gas Liquor from Gasification
Gas Liquor Oil / Tar Separation
Gas Liquor Gravel Filter
Phenol Extraction
Acid Gas Removal and Ammonia Recovery
Equalization Basin
Dissolved Air Flotation
Biological Oxidation-Extended Aeration
Sand Filtration
Activated Carbon Unit
Make up Water to Utilities Cooling Tower

Figure 3. Proposed wastewater management scheme for a Lurgi plant gasifying Illinois No. 6 bituminous coal (Continental Oil Company, 1979).

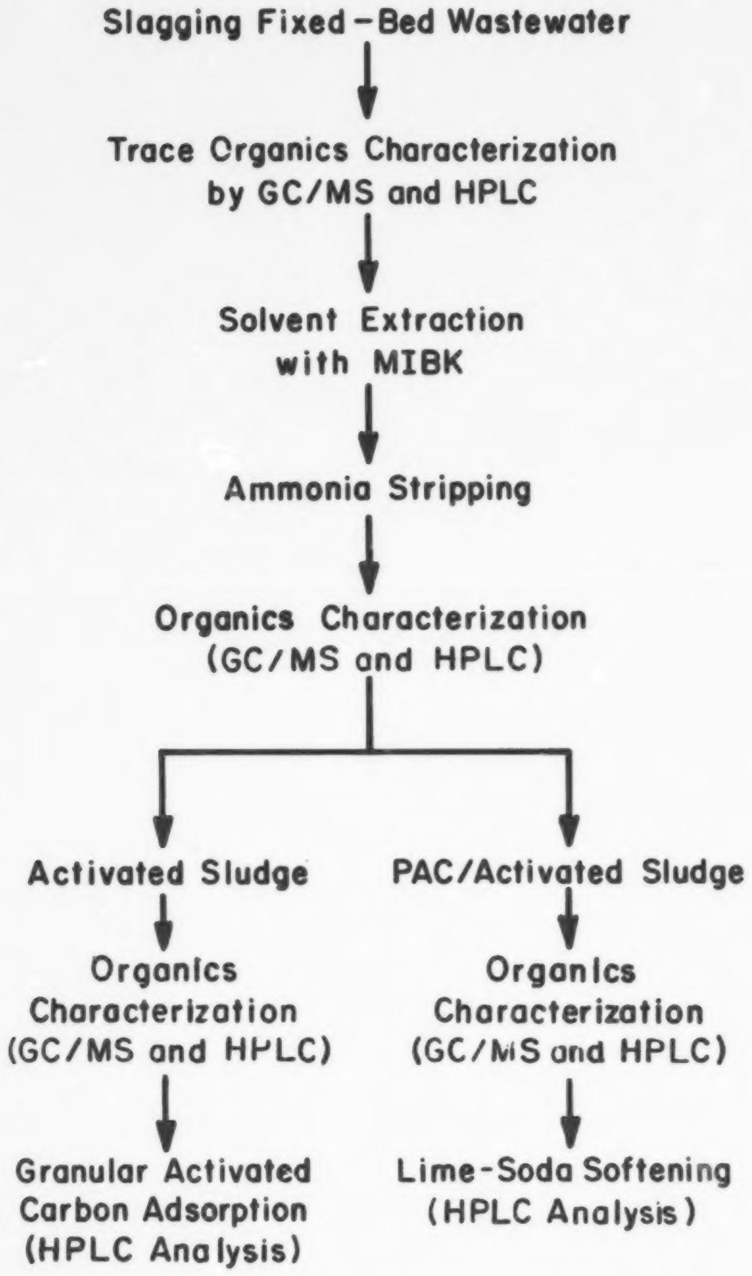
Slagging Fixed-Bed Wastewater
Trace Organics Characterization by GC/MS and HPLC
Solvent Extraction with MIBK
Ammonia Stripping
Organics Characterization (GC/MS and HPLC)
Activated Sludge
PAC/Activated Sludge
Organics Characterization (GC/MS and HPLC)
Organics Characterization (GC/MS and HPLC)
Granular Activated Carbon Adsorption (HPLC Analysis)
Lime-Soda Softening (HPLC Analysis)

Figure 4. Experiments in progress to evaluate essential features of a coal gasification wastewater treatment train.

type discussed above. This study utilizes GFETC slagging fixed-bed lignite wastewater without dilution. Wastewater is processed through solvent extraction, steam stripping, and biological oxidation with and without PAC addition. Effluent from biological oxidation with no PAC is treated by granular activated carbon adsorption, while effluent from the PAC-activated sludge reactor is evaluated for lime-soda softening characteristics. High pressure liquid chromatographic analyses are being performed after each treatment step to assess removal of polycyclic aromatic hydrocarbons. Screening GC/MS analyses are being conducted on raw, solvent extracted-ammonia stripped, and activated sludge and PAC-activated sludge effluent to characterize removal efficiencies for trace organic contaminants. At this writing, experiments have been completed through biological oxidation. Gas chromatography and GC/MS scans have been made for raw, solvent extracted-ammonia stripped, and PAC-actived sludge effluent. A report on the results of this investigation should be available for distribution later this year.

Several representative solvents were screened for use in the solvent extraction step. As a result of this analysis methylisobutyl ketone was selected for use owing to its measured high distribution coefficient for phenolics. Wastewater was processed through five sequential extraction steps at a solvent-to-liquid ratio of 1:15. This reduced phenolics from 5500 mg/l to about 5 mg/l. Concomitant with phenolics removal there was 88% reduction of COD (32,000 to 3900 mg/l) and 89% removal of BOD (26,000 to 2900 mg/l). Preliminary evaluation of GC/MS data suggests that there is on the order of 99%+ removal for most organic compounds through solvent extraction and ammonia stripping.

It has been demonstrated that solvent extracted wastewater can be processed by either activated sludge and PAC-activated sludge treatment without the need for dilution. Additionally, solvent extracted wastewater does not show tendency to foam excessively as observed in previous investigations. Effluent BOD values were in the range of 30 mg/l for both activated sludge and PAC-activated sludge treatment. PAC treatment showed generally better removal efficiency for TOC, COD, ammonia-nitrogen, organic-nitrogen, SCN^-, and color. Initial assessment of GC/MS scans of extracts from activated sludge and PAC-activated sludge treated wastewater indicates that organics are reduced to extremely low levels, generally less than several micrograms per liter.

This work has shown that solvent extraction offers several distinct wastewater processing advantages. Aside from recovering phenolics for use as a fuel or chemical commodity, there is achieved a marked reduction of trace organic compounds. If the extract is to be used for fuel, then there is the possibility of combusting toxic/hazardous organic compounds to thermal extinction. Solvent extraction reduces organic loading to a biological oxidation facility, and it may also serve as a physico-chemical treatment step to moderate shock loadings of organics. Solvent extracted coal gasification process wastewater is easier to treat biologically than wastewater which would otherwise contain much higher levels of organics.

FUTURE WORK

It is planned to continue these investigations in order to understand removal efficiencies and fates of trace organic compounds during treatment of wastewaters derived from production of synthetic fuels. Preparations are being made to perform experiments with slagging fixed-bed wastewater generated from conversion bituminous coal. Data gained from this study will be used to develop a model for predicting the fates of various trace organic contaminants during treatment with special emphasis on modeling removal of trace organics during solvent extraction. It is also proposed to conduct analogous investigations with oil shale and tar sand condensates where the objective of these studies would be to characterize and evaluate removal of organic compounds via proposed treatment trains for demonstration facilities.

ACKNOWLEDGMENTS

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PILOT PLANT EVALUATION OF H2S, COS, AND CO2 REMOVAL FROM CRUDE COAL GAS BY REFRIGERATED METHANOL

by

R. M. Kelly, R. W. Rousseau, and J. K. Ferrell

Acid gas removal systems are a necessary part of coal gasification processes. Carbon dioxide must be removed from gasifier product gas to improve the energy content of the gas and several sulfur compounds must be taken out to protect downstream process catalysts as well as reduce potential sulfur emissions.

At North Carolina State University, an integrated coal gasification- gas cleaning test facility is being used to study the environmental and process implications of several different acid gas removal solvents. Details of the plant facilities and operating procedures may be found in a recent EPA technical report (Ferrell et al., EPA-600/7-80-046a, March 1980) (1). This paper presents some of the initial results from acid gas removal pilot plant operation, discusses several aspects of methanol use for acid gas removal and outlines future experimental work on this part of the process.

INTRODUCTION

The choice of a solvent for acid gas removal in a coal gasification process depends upon several factors. Consideration must be given to the type of gasification scheme used, the sulfur content of the coal, the end use of the product gas and, most importantly, the process chosen for off-gas sulfur recovery. For both economic and environmental reasons, most large-scale coal gasification processes currently planned in the United States include some type of sulfur recovery unit. In general, the higher the sulfur content of the stream being sent to the recovery unit, the more favorable the economics. The type of solvent chosen, therefore, should exhibit some selectivity between the product gases, the sulfur compounds, and carbon dioxide.

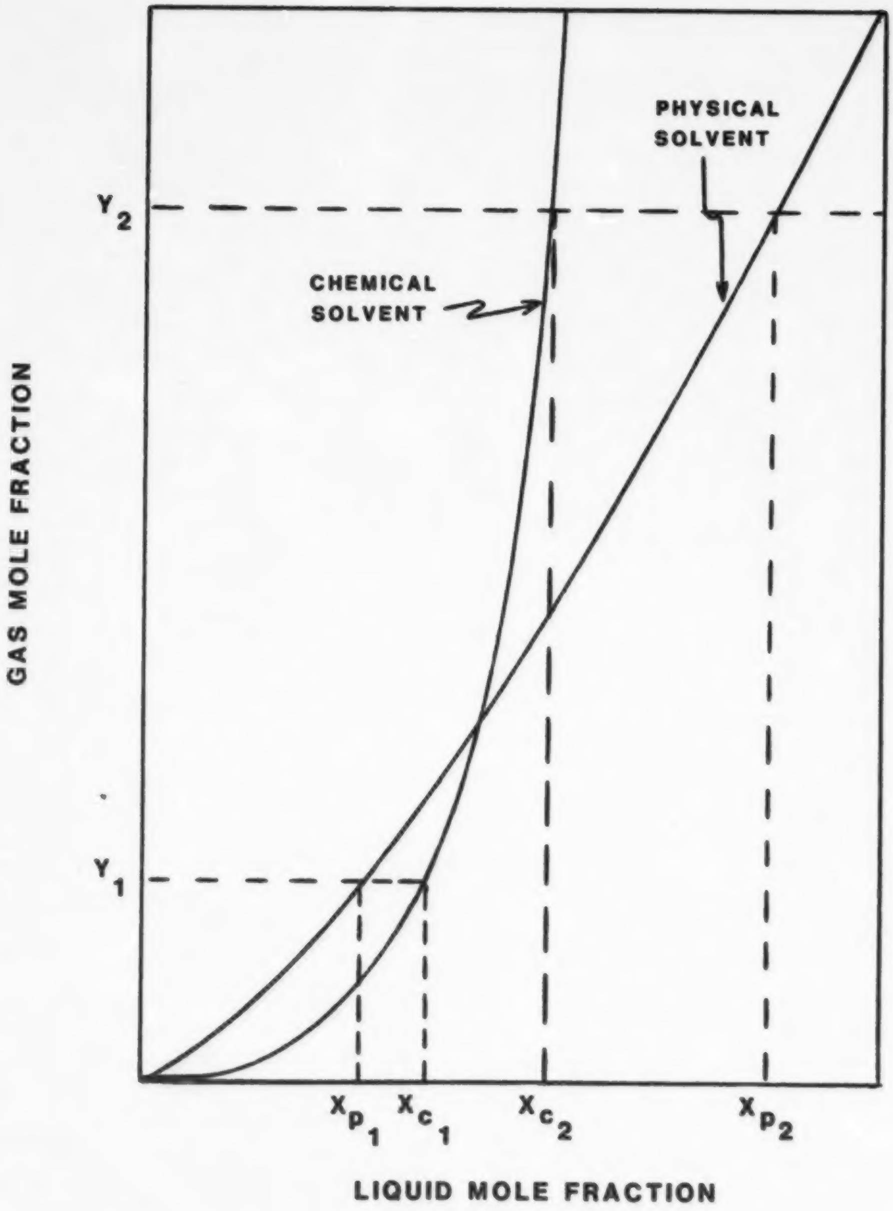
Both chemical and physical solvents have been considered for use in acid gas removal systems for coal gasification. The choice of one type of solvent over the other depends to a large extent on the partial pressure of the acid gases in the gas stream to be treated. Chemical solvents are preferred for low to moderate acid gas partial pressures, while physical solvents would be preferred at high acid gas partial pressures (see Figure 1). This basis of comparison reflects only the capacity of a particular type of solvent for acid gases and accounts neither for the selectivity between carbon dioxide and sulfur gases nor for the effectiveness of the solvent in treating specific sulfur compounds.

Very little information is available concerning the fate of certain sulfur compounds in either physical or chemical solvents. In a study undertaken to evaluate sulfur emission controls for the Western Gasification Company's coal gasification project in New Mexico, it was estimated that 1% of the total sulfur fed to a Lurgi gasifier would report as carbonyl sulfide. This takes on additional significance when considering that this represents almost 2.2 tons/day of sulfur(2). Because hydrogen sulfide and carbonyl sulfide are not absorbed/stripped with the same efficiency in most solvents, failure to account for each compound could result in unexpectedly high sulfur emissions.

As part of our research program, we plan to evaluate the effectiveness of both physical and chemical solvents in removing acid gases from both gasifier product gas and synthetic gas mixtures. Also, the build-up in the solvent of sulfur, nitrogen, and hydrocarbon species will be monitored. The results reported here are from experiments using a gas produced during fluidized bed gasification of Western Kentucky No. 11 coal char with emphasis on the fate of H2S and COS in the acid gas removal system.

FIGURE 1

EQUILIBRIUM DIAGRAM



PROCESS DESCRIPTION

Figure 2 shows a process flow sheet for the acid gas removal system (AGRS) used in this study. It was designed to operate with four different solvents:

1. refrigerated methanol

2. hot potassium carbonate

3. monoethanolamine

4. dimethyl ether of polyethylene glycol(DMPEG)

With minor modifications, other solvents could also be used. Feed gas from either the gasifier or from a mixing manifold can be used in making process measurements.

The AGRS consists of an absorber-flash tank-stripper combination with the necessary auxilliary equipment. The flash tank can be operated at pressures ranging from atmospheric to 28 atmospheres absolute. For good system performance, it is normally operated around 8 atmospheres absolute. The absorber and stripper are both packed columns, each containing three sections of packing, any or all of which can be used in mass transfer studies. Both are insulated and approach adiabatic operation. Operating ranges and column characteristics are given in Table 1.

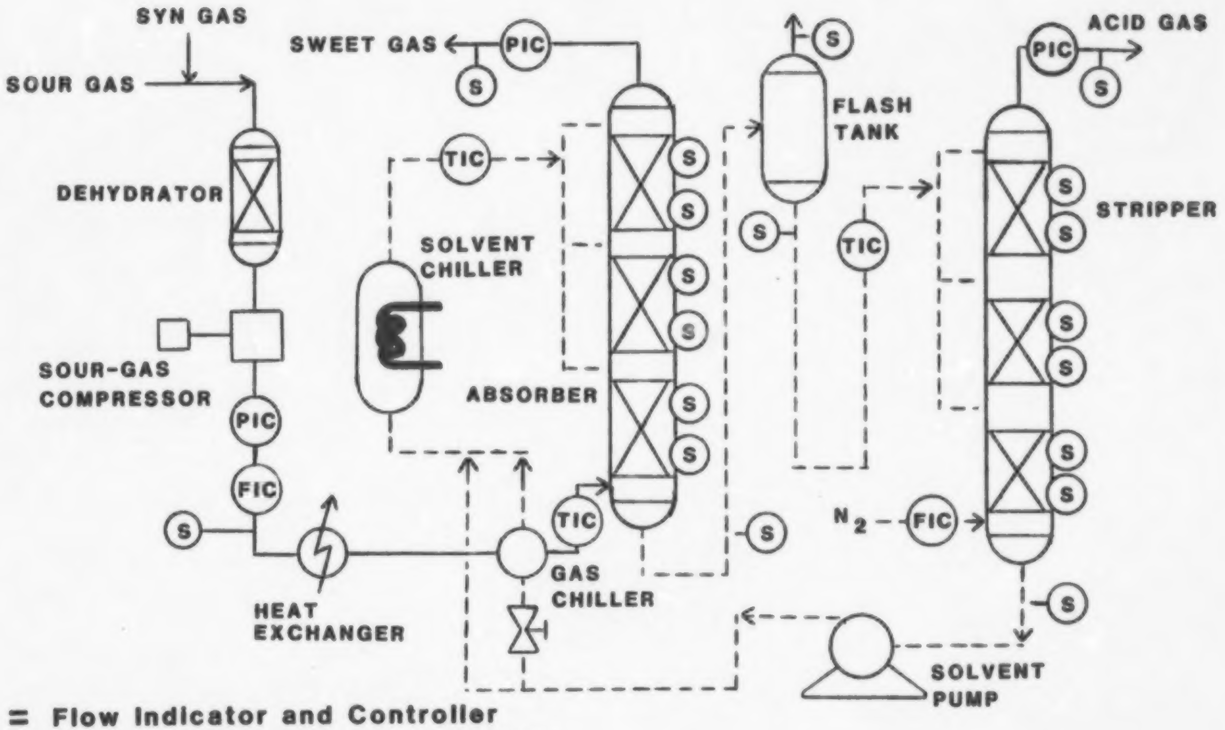
A refrigeration system provides sufficient cooling to feed methanol to the absorber at temperatures as low as 236 K (-35 F). Inert gas (nitrogen) is used to strip the methanol of acid gases but a reboiler is available for thermally stripping (regenerating) the chemical solvent systems.

Plant operation is monitored and regulated from a control room using graphical displays on a video terminal and a Honeywell TDC 2000 process control computer. Signals from 96 process sensors (temperatures, pressures, flow rates, and differential pressures) are sent to a PDP-11/34 plant data acquisition system.

All chemical analyses are done on the premises with occasional GC/ mass spectrometry done by EPA contractors. In the future, when the char used as gasifier feed is replaced by coal, the recirculating AGRS solvent will be checked for hydrocarbon build-up as well as for any trace materials of environmental or process signficance.

FIGURE 2

ACID GAS REMOVAL SYSTEM (AGRS)


SYN GAS
SOUR GAS
DEHYDRATOR
SOUR-GAS COMPRESSOR
PIC
FIC
S
HEAT EXCHANGER
SWEET GAS
PIC
S
TIC
SOLVENT CHILLER
ABSORBER
TIC
GAS CHILLER
S
FLASH TANK
TIC
ACID GAS
PIC
STRIPPER
N_2
FIC
SOLVENT PUMP

FIC = Flow Indicator and Controller
PIC = Pressure Indicator and Controller
TIC = Temperature Indicator and Controller
S = Sample Port

TABLE 1

COLUMN SPECIFICATIONS AND OPERATING RANGES FOR REFRIGERATED METHANOL

	Absorber	Stripper
Total Packed Height	21.3 ft	21.3 ft
column Diameter	5 inches	6 inches
No. of Packed Sections	3	3
Packing Type	Ceramic Intalox Saddles	Ceramic Intalox Saddles
Packing Size	1/4 inch	1/4 inch
Operating Temperature	-35 F to -10 F	-10 F to 60 F
Operating Pressure	100-500 psig	10-25 psig
Liquid Flow Rate	0.5-1.5 gpm	0.5-1.5 gpm
Gas Flow Rate	10-20 $\text{scfm}_{32°\text{F}}$	2-10 $\text{scfm}_{32°\text{F}}$

MASS BALANCE RESULTS

One of the major objectives of all initial runs was to achieve a closed material balance around the pilot plant. This required the ability to operate the plant at a steady state for long periods of time. Also, accurate flow measurements and chemical analyses are necessary as are proper sampling techniques.

A considerable amount of time was spent in improving mass balance closure so that deviations of less than 10% resulted. Because all flow streams were measured by orifice flow meters and laminar flow elements, calibrations had to correct for the effect of chemical composition on flow stream properties. To account for differences between the gas used for calibration and the process gas, a density correction was provided for orifice meter calibrations and a viscosity correction was provided for laminar flow element calibrations. These corrections were made to the flow rate measurements recorded by the data acquisition system and reported in a run summary.

While there is still room for improvement, the mass balance closure was adequate to reach some conclusions concerning the distribution of various compounds in the system. Improvement in the current mass balance closure will come from improved sampling techniques, especially for sulfur species, as well as better process control to enhance the quality of the steady state.

USE OF METHANOL AS AN ACID GAS REMOVAL SOLVENT

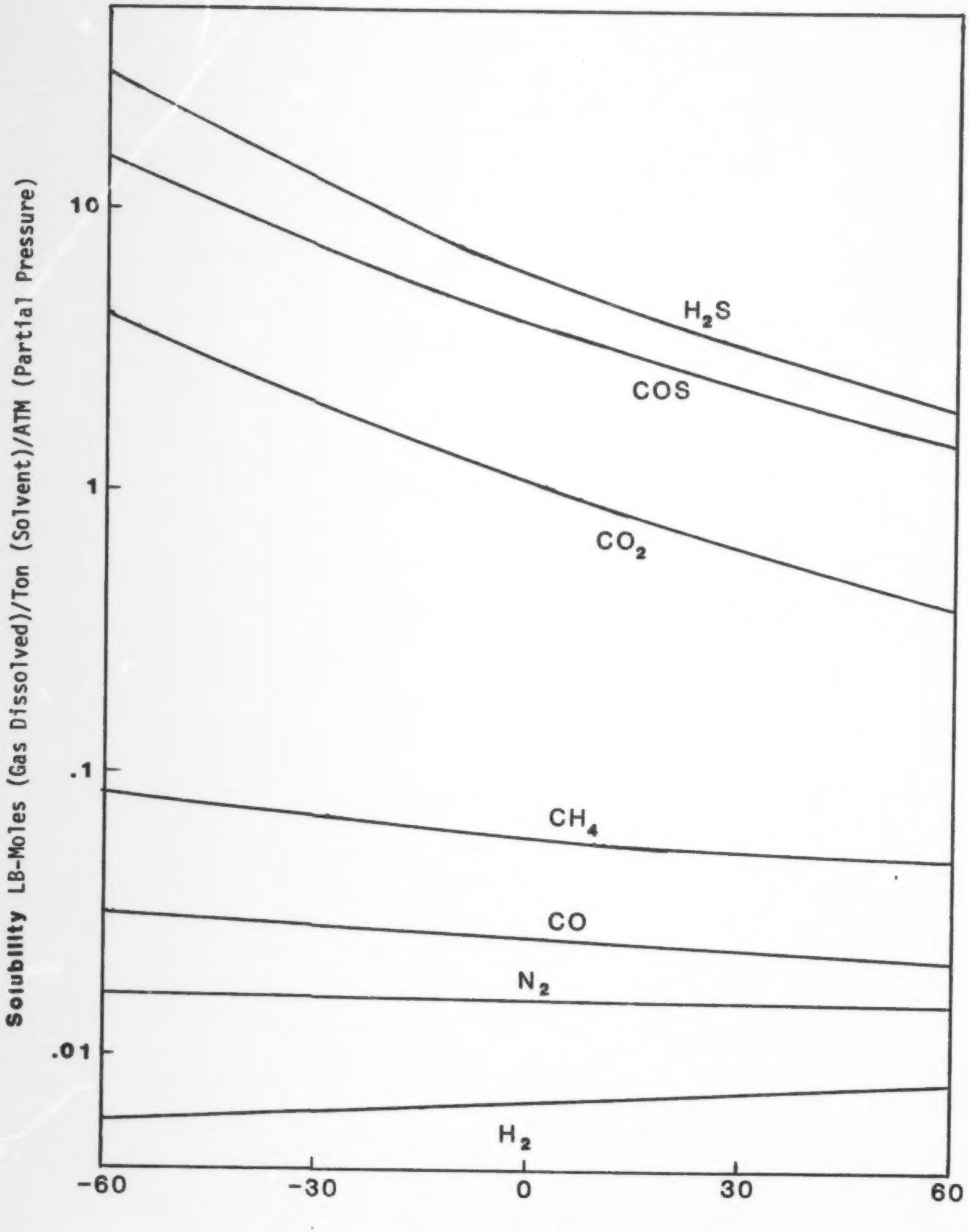
The choice of an acid gas removal system in coal gasification processes requires consideration of both process and economic factors. The residual levels of sulfur compounds and carbon dioxide, and their disposition in the AGRS, usually serve as the bases for decision. The options available include hot gas clean-up, direct conversion, physical and chemical solvents and no acid gas removal at all. Any process requiring the removal of both carbon dioxide and sulfur compounds at high acid gas partial pressures will probably use a physical solvent.

Although there are a score of proposed physical solvent processes for acid gas removal, only a few have been proven commercially. SELEXOL (DMPEG), developed by the Allied Chemical Corporation, and Rectisol (refrigerated methanol), developed by the Lurgi Corporation, are most frequently mentioned in coal gasification applications. Both are capable of achieving high degrees of carbon dioxide and sulfur gas removal and show sufficient selectivity for specific acid gases. The initial part of our study focused on the use of refrigerated methanol.

Figure 3 shows the solubilities of various gases in methanol as a function of temperature (3). This plot shows only the solubility of

FIGURE 3

SOLUBILITY OF GASES IN METHANOL (2)



each gas at a partial pressure of one atmosphere and does not reflect the thermodynamic non-idealities associated with the multicomponent system at higher pressures. Nevertheless, there are several points that can be made regarding the general behavior of these constituents in methanol.

In general, all gases shown here have an increased solubility with decreasing temperature and increasing partial pressure. Hydrogen and nitrogen are notable exceptions. Hydrogen solubility increases with temperature while nitrogen solubility is insensitive to temperature. The three acid gases (H_2S,COS,CO_2) are considerably more soluble than the other permanent gases and differ somewhat among themselves in solubility. At individual partial pressures of one atmosphere, the ratios of solubilities of various gases at a temperature of -40 F are shown in Table 2. Thus, one might conclude that the acid gases can be separated from the permanent gases and from each other given an appropriate separation scheme. In practice, however, thermodynamic factors and mass transfer restrictions make complete separation difficult.

Clearly, the evaluation of an acid gas removal system must consider both the ability of the solvent to remove acid gases to sufficiently low levels as well as its ability to separate carbon dioxide from the sulfur compounds. The absorber-flash tank-stripper combination used in this study cannot be operated to remove selectively the specific acid gases but removal efficiencies of each acid gas can be determined over a range of operating conditions. This information will then be used in developing a mathematical model to describe pilot plant operation and extended to predict both removal efficiencies and selectivity for other configurations. The necessary vapor-liquid equilibrium information is being developed in a parallel study and some results are already being used (4,5). Also, several pilot plant runs using synthetic gas mixtures are being used to determine process parameters. The final product of this study will be a computer simulation package useful in evaluating several process configurations for acid gas removal with methanol.

INITIAL RESULTS - REFRIGERATED METHANOL

Tables 3, 4, and 5 summarize some initial results of the current research program. It should be pointed out that the objective of these runs was not to remove as much of the acid gases as possible but rather to evaluate the effect of changing certain process variables on removal efficiencies. These runs represent a portion of a larger experimental program which is still in progress and will be the subject of a future report.

TABLE 2

RELATIVE SOLUBILITIES IN METHANOL AT -40°F (233K)

Gas	$\frac{\text{Solubility of Gas}}{\text{Solubility of } H_2}$	$\frac{\text{Solubility of Gas}}{\text{Solubility of } CO_2}$
H_2S	2540	5.9
COS	1555	3.6
CO_2	430	1.0
CH_4	12	
CO	5	
N_2	2.5	
H_2	1	

TABLE 3

OPERATING CONDITIONS

	30	35	36	37
Absorber				
Pressure (atm.abs.)	28.2	28.2	21.4	31.6
Height of Packing (ft)	7.1	7.1	7.1	21.3
Inlet Liquid Flow Rate $(\frac{16\ \text{moles}}{\text{hrft}^2})$	60.7	72.1	72.6	71.1
Inlet Liquid Temp. (°F)	-34.1	-36.3	-32.4	-36.3
Inlet Gas Flow Rate $(\frac{\text{lb moles}}{\text{hrft}^2})$	16.2	15.9	16.4	16.6
Inlet Gas Temp. (°F)	54.0	53.9	57.5	59.9
Flash Tank				
Pressure (atm. abs.)	7.8	7.8	7.8	7.8
Stripper				
Pressure (atm. abs.)	1.7	1.7	1.7	1.7
Height of Packing (ft)	21.3	21.3	21.3	21.3
Stripping N_2 flow $(\frac{\text{lb moles}}{\text{hrft}^2})$	0.9	0.9	0.9	0.9
Stripping N_2 Temp. (°F)	75.0	75.0	75.0	75.0

TABLE 4

RATIOS OF ACID GAS CONCENTRATIONS IN PROCESS STREAMS

Run #		Sour Gas	Sweet Gas	Flash Gas	Acid Gas
30	CO_2/H_2S	27.0	30.4	68.1	28.1
	H_2S/COS	21.7	16.0	14.7	21.7
	CO_2/COS	585.7	486.7	1004.7	611.1
35	CO_2/H_2S	34.7	25.7	80.7	36.4
	H_2S/COS	17.9	12.3	13.8	15.5
	CO_2/COS	622.4	316.7	1117.1	566.0
36	CO_2/H_2S	23.4	6.2	59.3	31.4
	H_2S/COS	18.6	17.0	15.0	16.7
	CO_2/COS	435.4	105.0	887.6	524.0
37	CO_2/H_2S	29.0	15.6	76.1	31.4
	H_2S/COS	18.4	13.7	14.6	17.4
	CO_2/COS	533.0	213.3	1112.1	546.5

TABLE 5

ABSORBER OPERATION

	30	35	36	37
Pressure (atm absolute)	28.2	28.2	21.4	31.6
Ht. of packing (ft)	7.1	7.1	7.1	21.3
L in (# moles/hr-ft^2)	60.7	72.1	72.6	71.1
G in (# moles/hr-ft^2)	16.2	15.9	16.4	16.6
G out (# moles/hr-ft^2)	11.5	11.4	12.8	12.1
T_L in (°F)	-34.1	-36.3	-32.4	-36.3
T_L out (°F)	3.5	-0.6	-1.7	7.2
T_G in (°F)	54.0	53.9	57.5	59.9
Liquid Temperature rise (°F)	37.6	35.7	30.7	43.5
H_2S in (ppm)	9096	8072	8918	8631
H_2S out (ppm)	476	371	682	405
% removed	96.3	96.7	94.0	96.7
COS in (ppm)	423	449	476	475
COS out (ppm)	32	34	37	27
% removed	94.3	94.5	94.2	95.8
CO_2 in (%)	24.6	28.0	20.9	25.1
CO_2 out (%)	1.5	1.0	0.4	0.6
% removed	95.8	97.6	98.4	98.1

Mass balance reports for the runs listed in Tables 3, 4, 5 are included in the Appendix.

In general, AGRS balances meet the established criteria of less than a 10% deviation from complete closure. In cases where more than a 10% deviation was measured, flow meter and chemical analysis problems have been cited and will be corrected in future runs. Because solvent losses are an important consideration in using methanol, this analysis has recently been incorporated into the research program and results are reported in runs 35 and 37. This will be done routinely in the future. Failure to account for methanol losses in the gas exiting the flash tank and in the acid gas stream is probably a factor in mass balance overestimation.

Calculated liquid compositions exiting each vessel are reported as determined by difference. In the past, liquid samples between columns and at the stripper exit were taken as were samples from the column packing. Sampling and analytical problems led to the temporary abandonment of this practice but it will be reinstated in the future. The liquid exiting the stripper, however, is usually sampled and analyzed for residual acid gases. A check was also made of the hydrocarbon content of the solvent after approximately 60 hours of operation. No detectable hydrocarbons were found which is not a suprising result considering the fact that char and not coal was used as a feedstock to the gasifier (6). Future experiments call for the gasification of coal-char mixtures where the build-up of hydrocarbons in the methanol will be monitored and compared to the results obtained for char gasification.

The results presented here are from the clean-up of gases generated by the gasification of Western Kentucky No. 11 bituminous coal char. This char contains very little volatile matter (less than 2.0%) so that the sulfur gases produced will generally be the product of the gas phase hydrolysis of H2S, the predominant sulfur gas form. This means that most of the sulfur gases fed to the AGRS will be in the form of H2S, COS, with small amounts of CS2. Traces of methyl mercaptan, ethyl mercaptan, methyl sulfide and thiophene were also found in some gas streams but their irregular appearance prevent any quantitative conclusions concerning their distribution in the AGRS. These sulfur species are probably related to the volatile matter present in the feed char. Present efforts include a more detailed look at the fate of the less concentrated sulfur species.

DISCUSSION OF RESULTS

1. System Performance

The results presented in Tables 3, 4, 5 and in the Appendix represent system performance for a series of runs made at fairly low liquid to gas (L/G) ratios. These results verify the expected order of solubility for the three acid gases in methanol and show how these gases distribute in the acid gas removal system. Although the system is considerably simpler than a commercial process, it does contain the three basic unit operations (absorption, flash vaporization, and stripping) found in the Rectisol process.

Overall system performance can be discussed using run AM-30 as an example. This run was made using 7.1 feet of packing in the absorption column and 21.3 feet of packing in the stripper. Because current emphasis is on absorber operation, each of the four runs shown here utilized the total packed height of the stripper so that esentially clean methanol could be fed to the absorber. This was verified through the analysis of the methanol leaving the stripper.

The mass balance report of AM-30 shows that each compound, with the exception of CO2, was within 4.0% of complete closure. The CO2 balance offset can be traced to flow meter calibration problems for the Acid Gas stream and also to failure to account for the methanol present in this stream. This problem also appeared in runs 36 and 37 and has been corrected for future runs. A mass balance of this quality gives added significance to the results obtained especially for the sulfur compounds. Methanol analyses of the three exiting gas streams were not done for this run, but other runs showed negligible amounts in the Sweet Gas with the concentration increasing for the Flash Gas and the Acid Gas. The increased presence of methanol in these streams was expected because they are at decreased pressure and increased temperature.

The choice of the operating pressure for the flash tank is based on several factors. The Rectisol process contains a series of flashing operations designed to remove the acid gases from the solvent and allow for some separation of the sulfur compounds from CO2. In our system, operation at moderate pressures (4.4-11.2 atm. abs.) provides some insight into how these gases distribute. Also, flash tank operation indicates how closely our vapor- liquid equilibrium model predicts actual system performance. Moderately high pressures are a better test as to how well the VLE model handles departures from ideal behavior. Finally, trial and error has shown that this range of operating pressures is more compatible with overall system performance; the effect of process controller oscillation on sampling and steady state operation is reduced.

Stripper operating pressure was 1.7 atmospheres absolute for AM-30 and for the three other runs. In practice, stripper operating conditions are the result of a balance between temperature and pressure to minimize solvent losses and yet regenerate the solvent. The pressure used here represents the lowest that the stripper pressure controller could maintain and still avoid the adverse influence of process controller oscillation. Inlet temperature to the stripper was not controlled but will be used later to facilitate stripper simulation efforts.

Since the focus of these runs in on absorber performance, column pressure was varied along with liquid flow rate and inlet liquid temperature. Variation in Sour Gas CO2 concentration introduced additional variation demonstrating the necessity for a mathematical model in process analysis. The model is described further in the next section.

The temperatures measured throughout the acid gas removal system are very important in terms of understanding the process. Since the sampling of liquid and gas from the column packing proved to be unsuccessful, column temperature profiles take on added significance in determining mass transfer rates. Current modeling efforts rely on comparisons of measured and predicted column temperature profiles. This profile is indicative of the rate of CO2 transfer because of the large heat effects associated with CO2 absorption in methanol.

The absorber temperature profiles are reported in the Appendix for all four runs and were measured with sensors located on the outside of the absorption column wall. For all runs, temperature sensor TT350, located at 4.8 feet above both the gas inlet and the bottom of the packing, did not stay fastened to the column wall and is probably inaccurate. In addition, the lowest temperature measured, TT353, at 0.3 feet, is probably located too close to the packing end and therefore not useful. These will be moved for future runs.

Both height of packing and height above the gas inlet are reported to point out that end effects have been minimized. In earlier runs, the gas inlet was located 7 inches below the bottom of the packing and significant end effects were observed in those runs. Because it is important in the modeling efforts to eliminate end effects, the bottom of the absorber was reconstructed to ensure that the mass transfer takes place in the column packing and not above or below it.

An interesting observation can be made concerning the temperature profile of the stripper. At the top of the column, the acid gases flash due to the pressure reduction of the solvent entering from the flash tank. This can be noted from the decreasing temperatures measured in the top part of the column. Further down the column, the temperature begins to increase as the influence of the warm stripping nitrogen is felt. A lower flash tank pressure would reduce this flashing effect as the pressure drop between the flash tank and the stripper would be less.

2. Acid Gas Distribution in the AGRS

Table 4 shows the ratios of acid gas concentrations for the various gas streams in the AGRS. The ratios of the acid gases exiting the stripper in the concentrated Acid Gas stream are the same as those in the entering Sour Gas stream. This is the expected result for non-selective physical solvent systems.

Because of problems with the analysis of low levels of CO2 in the Sweet Gas stream, not much can be said of the ratios involving CO2. However, it appears that H2S is removed at a slightly higher efficiency than COS when the ratios in the Sour Gas stream are compared to the

Sweet Gas stream. This is expected because H2S has a slightly higher solubility than COS over the temperature range used.

The Flash Gas ratios reflect the amount of CO2 initially fed to the system. Here, the ratios of CO2 to H2S and COS are about twice those found in the entering Sour Gas stream. Changing the flash tank operating presures would improve this selectivity. This indicates that there is the potential to concentrate the CO2 fed to the system through a flashing process. The ratio of the sulfur compounds (H2S:COS) is again less than that found in the Sour Gas. The fact that H2S is more soluble than COS means that proportionately less H2S will flash upon pressure reduction.

3. Absorber Column Performance

Table 5 contains the results associated with absorber column performance for four integrated runs treating a gas produced in the gasifier. An attempt was made to vary system conditions to show the effect on acid gas removal efficiencies. A comparison of the results from these runs underline the importance of mathematical modeling to analyze system performance.

All runs show an acid gas removal efficiency of at least 94.0% for the range of operating conditions used. Also, only small differences in component removal efficiencies can be seen despite the changes in packed height, liquid flow rate, and operating pressure. The reason for this can be explained by examining the inlet gas compositions for each run and by considering mass transfer limitations.

Gasifier operation will dictate both the composition and flow rate of the gas stream fed to the AGRS. For the four runs shown here, the inlet gas flow rate to the absorber varied only slightly but the CO2 content of the stream varied significantly. This affects the absorber column temperature profile as the magnitude of the absorption heat effect depends on the amount of CO2 absorbed. As the temperature increases, the amount of acid gases removed decreases.

This effect can be seen by comparing the results of runs 35 and 36 in Table 5. Although 35 was made at a higher absorber pressure and lower inlet liquid temperature, the acid gas removal efficiencies are approximately the same. A closer look shows that there is 7% more CO2 in the entering gas stream for run 35. The increased thermal effect tends to offset the expected increase in column removal efficiency.

Run 37, made with three times the packed height used in the other runs, resulted in only small improvements in acid gas removal efficiency. This indicates that for the range of operating conditions used, acid gas removal efficiency has reached an upper limit. improvements could be obtained with lower inlet temperatures, higher operating pressures and larger liquid flow rates.

The effect of changing liquid flow rates can be seen by comparing runs 30 and 35. The increase in the liquid flow rate from 60.7

lb-moles/hr/sq.ft. to 72.1 lb-moles/hr/sq.ft. improved CO2 removal efficiency by 1.8%. H2S and COS removal remained about the same probably because of mass transfer limitations. Future runs will be made at higher L/G ratios to examine more completely the effect of this variable on removal efficiency.

The results from these four runs clearly point to the need to develop a mathematical model to assist with the analysis of experimental results and provide a basis for analyzing more complicated process configurations. Although there exists the possibility of feeding synthetic gas streams to the AGRS, the most useful information comes from runs where gasifier product gas is used. Because of the variability associated with gasifier operation, a carefully structured experimental plan would be difficult to complete. The strategy used thus far has been to cover a wide range of operating conditions. Then, a mathematical model will be used to extend these results to process situations that cannot be studied with the pilot plant.

PROCESS MODELING

At present, mathematical modeling efforts have mainly dealt with describing the operation of the packed absorption column for the adiabatic case. A calculational technique first described by Feintuch and Treybal (7,8) for packed column design has been implemented on the computer and is currently used for analyzing runs where synthetic gas mixtures of carbon dioxide and nitrogen are fed to the absorption column. Thus far, only cases for the absorption of a single component have been modeled but a multicomponent case is currently being developed to describe the transfer of H2S, COS, CS2, CO2, H2, N2, CO, and CH4. Additional hydrocarbons will be added to this list as the experimental program moves into the gasification of coal-char mixtures.

The calculational technique described accounts for the mass and heat transfer resistances in both the liquid and gas phases. Solvent evaporation is also incorporated into the calculation. It is an essentially rigorous solution to a highly non-linear set of partial differential equations which treats a packed column as a true differential device without resorting to a stage -wise, tray tower analogy (8). The method involves dividing the tower height into differential sections and satisfying heat transfer, mass transfer, and equilibrium relationships for each section. Experimental verification of this technique for air-water-ammonia systems at ambient pressure and temperature has been shown by Raal and Khurana (9). Feintuch (8) suggests an extension of this technique to complex multicomponent systems but no literature data are available with which to compare the results. Initial indications from our work indicate that this calculational method applies to the multicomponent system studied here.

As a first step in model development, computer simulation for the adiabatic absorption of CO2 in methanol was tried. Results for a recent synthetic gas run (AM-32) are presented in Figure 4. Here, the liquid temperature profile in the absorber is compared to the model prediction. Process conditions for AM-32 are shown in Table 6. Thus far, excellent agreement between model prediction and experimental data has been seen for column temperature profiles and removal efficiencies. The model also predicts both liquid and gas flow rate and composition profiles for both design and analysis approaches to packed column performance. The model has been used for simulation of systems containing H2S-N2- CH3OH and COS-N2-CH3OH. A multicomponent case is presently being developed for the components mentioned above. An upcoming EPA technical report will provide a more detailed description of mathematical modelng efforts.

FUTURE EXPERIMENTAL WORK

Figure 5 and Table 7 illustrate the present scope of our research program and plans for future work. Currently, we anticipate using a chemical solvent following the evaluation of refrigerated methanol and should begin this work sometime during 1981. A full evaluation of each solvent used includes experimental runs with both crude coal gas and synthetic gas mixtures. A computer simulation package for each system is planned. Also, vapor-liquid equilibrium model development will parallel all anticipated pilot plant studies. Capability to measure both binary and multicomponent VLE information exists and has already been utilized. This collection of information, along with an assessment of the fate of certain trace compounds, should provide the basis for evaluating the relative merits of the solvents proposed for acid gas removal in coal gasification processes.

FIGURE 4

PACKED ABSORPTION COLUMN LIQUID TEMPERATURE PROFILE FOR SYNGAS RUN AM-32

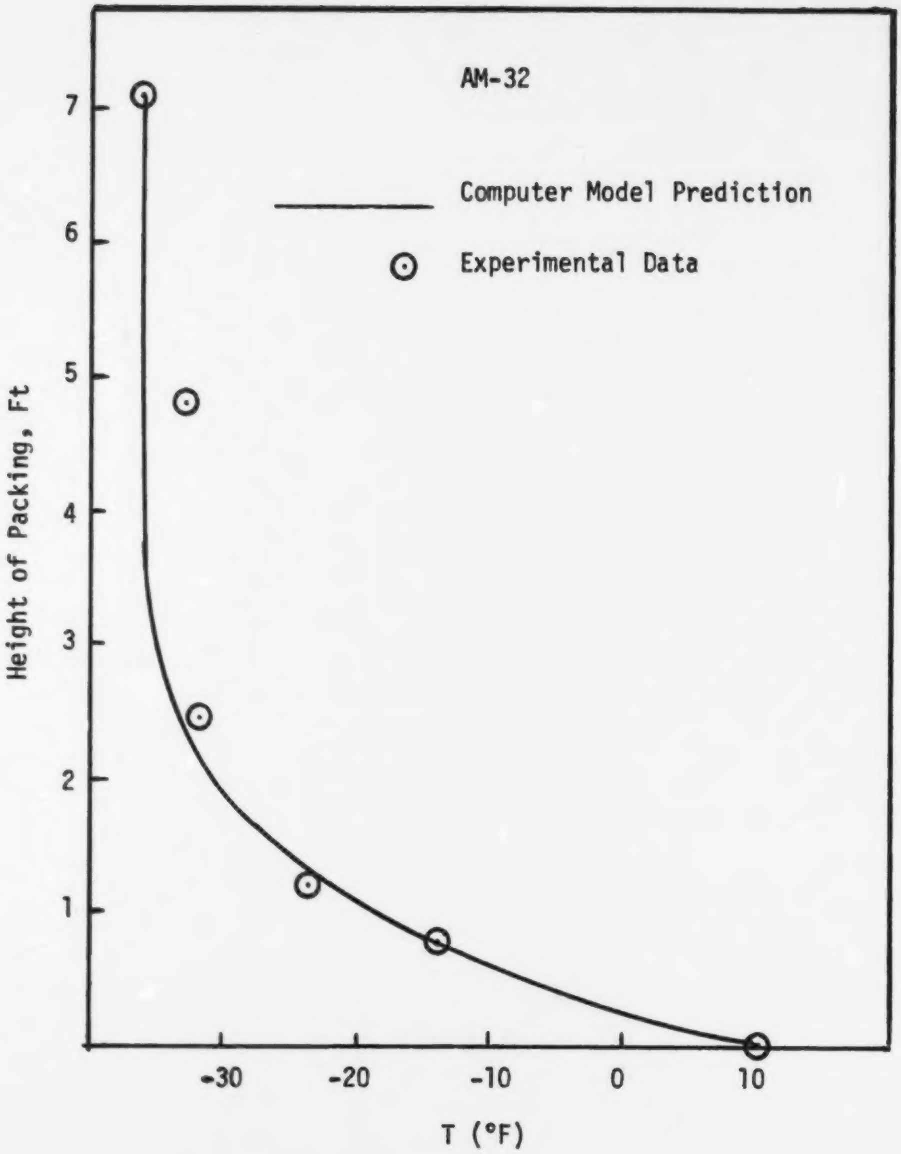


TABLE 6

PROCESS CONDITIONS FOR SYNTHETIC GAS RUN AM-32

Liquid Flow Rate	61.05 lb moles/hr/ft^2
T_L in	-36.1°F
Gas Flow Rate	17.31 lb moles/hr/ft^2
T_G in	57.4°F
Pressure	28.0 Atmospheres absolute
Inlet Gas Composition	33.73 mole percent CO_2 66.27 mole percent N_2
Outlet Gas Composition	0.92 mole percent CO_2 99.08 mole percent N_2
CO_2 Removal Efficiency	98.10%

FIGURE 5

AGRS RESEARCH PROGRAM

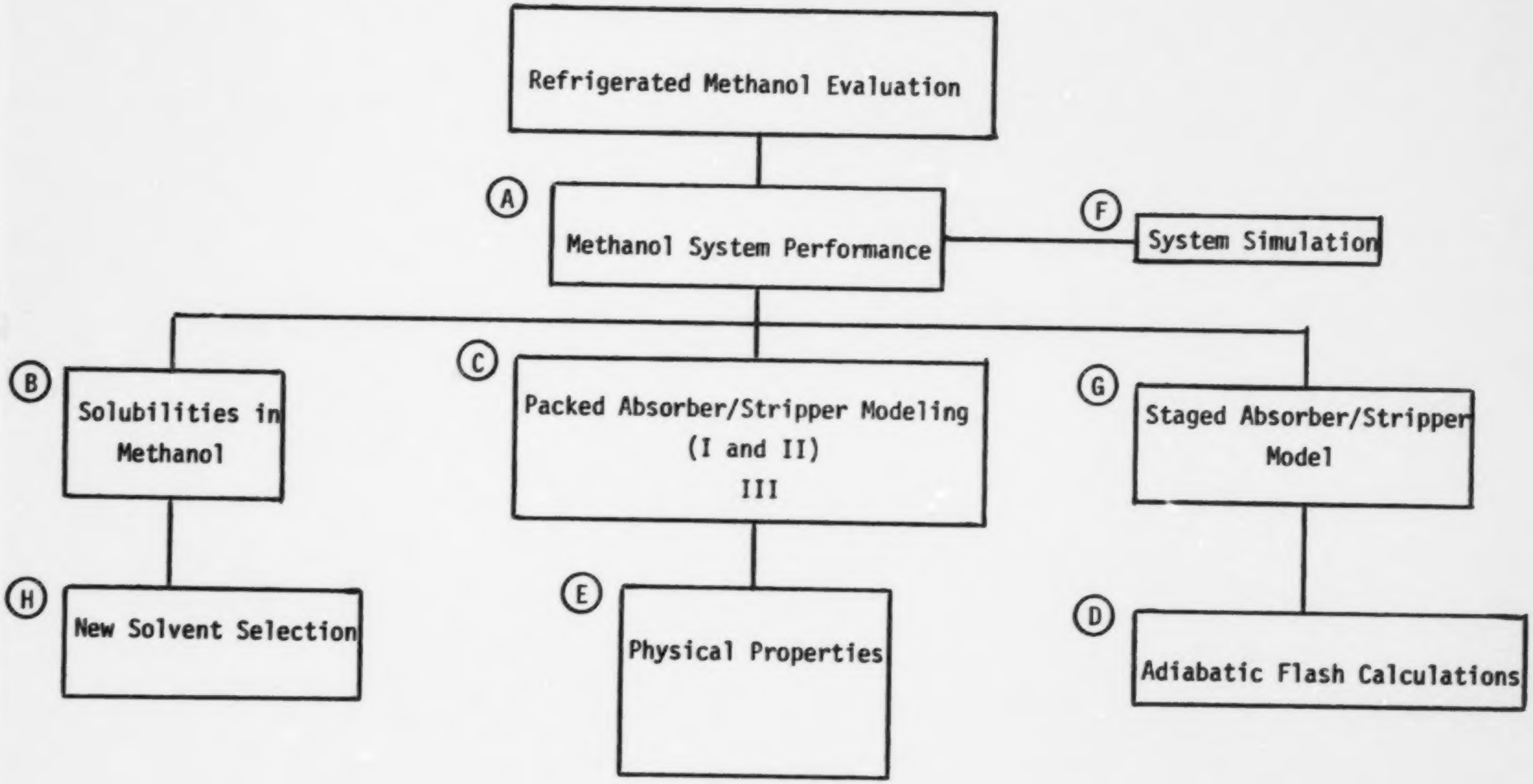

Refrigerated Methanol Evaluation
Ⓐ
Methanol System Performance
Ⓕ
System Simulation
Ⓑ
Solubilities in Methanol
Ⓒ
Packed Absorber/Stripper Modeling (I and II) III
Ⓖ
Staged Absorber/Stripper Model
Ⓗ
New Solvent Selection
Ⓔ
Physical Properties
Ⓓ
Adiabatic Flash Calculations

TABLE 7

A. Methanol System Performance

1. CO_2, H_2S, COS and other sulfur gas removal
2. Hydrocarbons, particularly aromatics, removal and accumulation in solvent
3. Thermal behavior
4. Relationship of gasifier operation to AGRS performance
5. Comparison of SYNGAS and crude coal gas operations
6. Methanol losses from absorber, flash tank and stripper
7. Solvent stability

B. Solubilities in Methanol

1. Use current VLE model (Ferrell, Rousseau and Matange, 1980) in absorber/stripper/flash tank calculations
2. Use current VLE model to develop methods for calculating heats of solution
3. Obtain VLE data on COS, CS_2, and other important gases, and incorporate into VLE model
4. Modify current model to use Wilson and/or UNIQUAC equations

C. Packed Absorber/Stripper Models I, II, and III

Model I (SIMPAK): considers a three-component system in which the carrier gas is insoluble

Model II (MCOMP): places no restrictions on number of components or solubility of carrier gas

Model III (von Stockar method): relies on an unsteady state description of the packed column, and is believed to have better convergence properties than approach of Model I and II

1. Model development for packed columns
2. Use of model in simulation of SYNGAS operation

3. Use of model in evaluation of crude coal gas operation

4. Use of model to guide selection of AGRS operating variables (e.g. N2 flow rate to stripper to maximize sulfur concentration of feed stream to sulfur recovery unit.)

D. Adiabatic Flash Calculation

1. Model flash tank in AGRS

2. Describe flashing process as liquid enters stripper

E. Physical Properties and Equipment Parameters

1. Document, catalog and make available all physical properties, diffusivities and packing characteristics used in system

F. System Simulation

1. Bring all system elements together in a program to examine unit interactions and optimize operating conditions

G. Staged Absorber/Stripper Model

1. Extension of Packed column models to staged columns to provide necessary tools for system simulation

H. New Solvent Selection

1. Begin to consider next solvent system to study (e.g. hot potassium carbonate) and determine needed information to begin evaluation

2. Determine advantages/disadvantages of potential solvents

3. Provide basis for choosing desirable features of acid gas removal solvents from environmental, process, and energy considerations

REFERENCES

(1) Ferrell, J. K., R. M. Felder, R. W. Rousseau, J. C. McCue, and R. M. Kelly, "Coal Gasification/Gas Cleanup Test Facility: Volume I. Description and Operation," EPA-600/7-80-046a, March 1980).

(2) Beychok, Milton R.,"Sulfur Emission Controls for a Coal Gasification Plant," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, II, (Hollywood, Florida - 1975), EPA-600/2-76-149, June 1976.

(3) Ranke, Gerhard, "The Rectisol Process- for the Selective Removal of CO2 and Sulfur Compounds from Industrial Gases," Chemical Economy and Engineering Review, Vol. 4 (1972), pp. 25-31.

(4) Ferrell, J. K., R. W. Rousseau, and D. G. Bass, "The Solubility of Acid Gases in Methanol," EPA-600/7-79-097, April 1979.

(5) Ferrell, J. K., R. W. Rousseau , and J. N. Matange, "The Solubility of Acid Gases and Nitrogen in Refrigerated Methanol," EPA-600/ 7-80-116 May 1980.

(6) Private communication with Dr. Santosh Gangwal, Process Engineering Department, Research Triangle Institute, Durham, North Carolina, (July 1980).

(7) Treybal, R. E., "Adiabatic Gas Absorption and Stripping in Packed Towers," Industrial Engineering Chemistry, Vol. 61 (1969), p. 36.

(8) Feintuch, H. M., and R. E. Treybal, "The Design of Adiabatic Packed Towers for Gas Absorption and Stripping," Industrial Engineering Chemistry Process Design and Development, Vol. 17 (1978), pp. 505-514.

(9) Raal, J. D., and M. K. Khurana, "Gas Absorption with Large Heat Effects in Packed Columns," The Canadian Journal of Chemical Engineering, Vol.51 (1973), pp. 162-167.

APPENDIX

AM-30

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$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
$                                          $
$ NCSU DEPARTMENT OF CHEMICAL ENGINEERING  $
$                                          $
$      ACID   GAS   REMOVAL   SYSTEM       $
$                                          $
$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$


                         RUN NUMBER A-M-30
                          INTEGRATED
                         DATE     5/28/1980


                      STREAM COMPOSITION (MOL %)
                      ------ -----------

                                                                       $           $          $
       SOUR GAS   SWEETGAS   FLASHGAS   STRIPN2   ACID GAS   ABSORBOT   FLASHBOT   STRIPBOT

CO2     24.600      1.460     43.200      0.000    71.500      5.918      5.545      0.000
H2S      0.910      0.048      0.634      0.000     2.539      0.220      0.216      0.000
COS      0.042      0.003      0.043      0.000     0.117      0.010      0.010      0.000
MEOH     0.000      0.000      0.000      0.000     0.000     92.764     93.669     99.498
H2      33.170     43.190     15.240      0.000     0.000      0.619      0.473      0.502
CO      21.060     28.480     22.720      0.000     1.020      0.204      0.000      0.000
N2      18.500     24.890     14.750    100.000    24.560      0.202      0.057      0.000
CH4      1.640      1.950      3.400      0.000     0.420      0.064      0.030      0.000


                      $
                       CALCULATED


                     MASS BALANCE (LB-MOLES/HR)
                     ---- -------


                 IN                          OUT
                 --                          ---

                                                                          $            $
       SOUR GAS   STRIP N2      SWEETGAS   FLASHGAS   ACID GAS     TOTAL IN   TOTAL OUT   % RECOVERY
CO2     0.554      0.000         0.023      0.038      0.550        0.554      0.611        110.3
H2S     0.020      0.000         0.001      0.001      0.020        0.020      0.021        101.7
COS     0.001      0.000         0.000      0.000      0.001        0.001      0.001        104.0
MEOH    0.000      0.000         0.000      0.000      0.000        0.000      0.000          0.0
H2      0.747      0.000         0.692      0.013      0.000        0.747      0.705         94.4
CO      0.474      0.000         0.456      0.020      0.008        0.474      0.484        102.0
N2      0.417      0.182         0.399      0.013      0.189        0.599      0.601        100.3
CH4     0.037      0.000         0.031      0.003      0.003        0.037      0.037        101.4

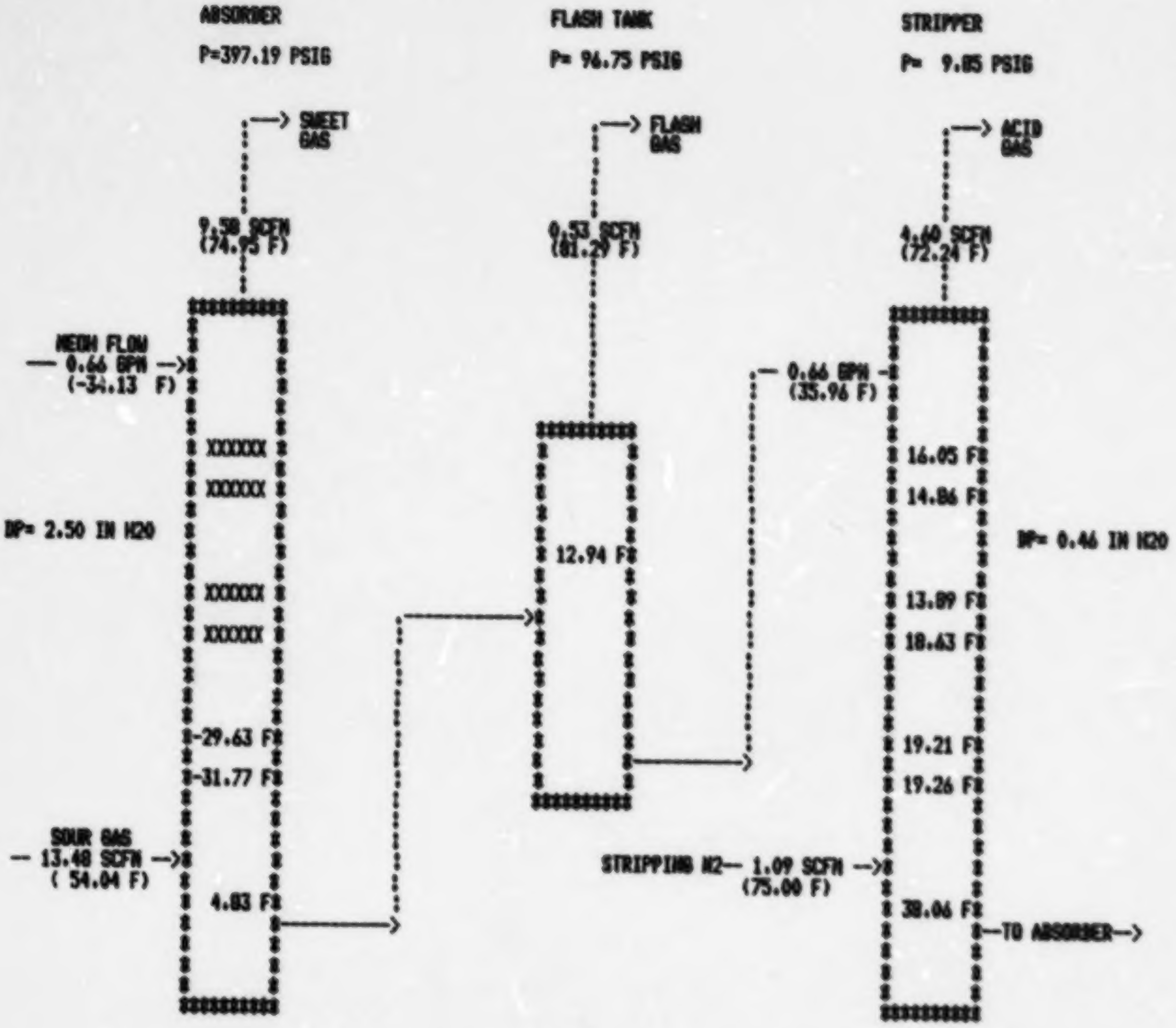
TOTAL   2.253      0.182         1.602      0.089      0.769        2.433      2.461        101.130
(LB-MOLES/HR)


                      $
                       METHANOL-FREE BASIS


          TOTAL METHANOL LOSS=  0.000 LB-MOLES/HR =  0.000 GALLONS/HR
```

RUN NUMBER A-M-30
INTEGRATED
DATE 5/28/1980

COLUMN TEMPERATURE PROFILES & MASS BALANCES


ABSORBER
P=397.19 PSIG
SWEET GAS
9.50 SCFM
(74.95 F)
MEOH FLOW
0.66 GPM
(-34.13 F)
XXXXXX
XXXXXX
DP= 2.50 IN H2O
XXXXXX
XXXXXX
-29.63 F
-31.77 F
SOUR GAS
13.48 SCFM
(54.04 F)
4.83 F
FLASH TANK
P= 96.75 PSIG
FLASH GAS
0.53 SCFM
(81.29 F)
12.94 F
STRIPPER
P= 9.85 PSIG
ACID GAS
4.60 SCFM
(72.24 F)
0.66 GPM
(35.96 F)
16.05 F
14.86 F
DP= 0.46 IN H2O
13.89 F
18.63 F
19.21 F
19.26 F
STRIPPING N2— 1.09 SCFM
(75.00 F)
38.06 F
TO ABSORBER

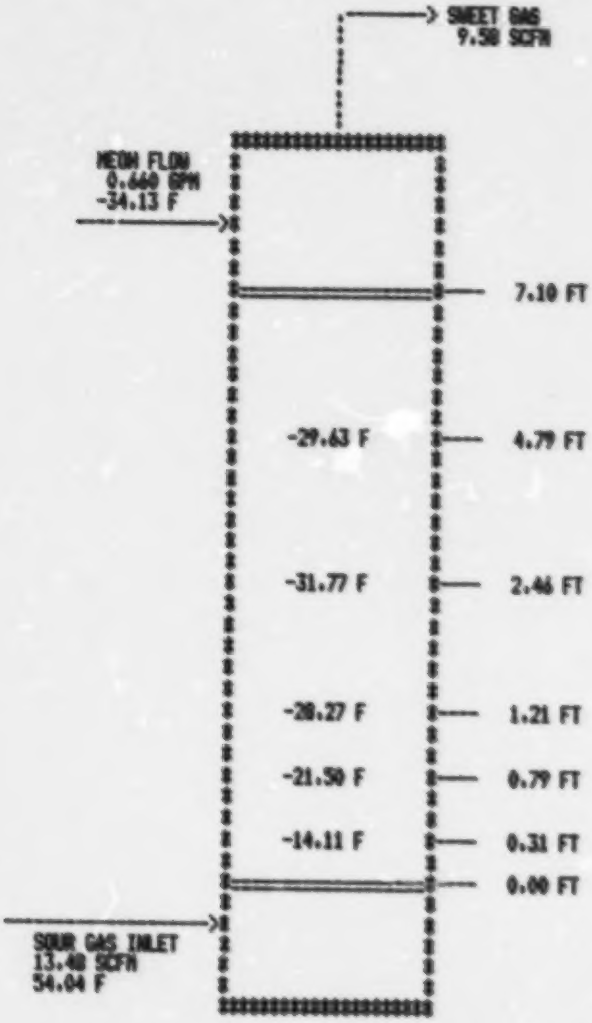
RUN NUMBER A-H-30
INTEGRATED
DATE 5/28/1980

COLUMN TEMPERATURE PROFILE

ABSORBER COLUMN PRESSURE =397.2 PSIG

TOTAL PACKING HEIGHT= 7.10 FEET

PACKING USED = 1/4" CERAMIC INTALOX SADDLES


SWEET GAS
9.58 SCFM
MEOH FLOW
0.660 GPM
-34.13 F
7.10 FT
-29.63 F
4.79 FT
-31.77 F
2.46 FT
-28.27 F
1.21 FT
-21.50 F
0.79 FT
-14.11 F
0.31 FT
0.00 FT
SOUR GAS INLET
13.48 SCFM
54.04 F

TRANSMITTER	HEIGHT ABOVE GAS INLET	HEIGHT OF PACKING	TEMPERATURE(F)
TT350	4.79	4.79	-29.63
TT351	2.46	2.46	-31.77
TT352	1.21	1.21	-28.27
TT353	0.31	0.31	-14.11
TT354	0.79	0.79	-21.50

AM-35

```
*********************************************
*                                           *
* NCSU DEPARTMENT OF CHEMICAL ENGINEERING   *
*                                           *
*       ACID   GAS   REMOVAL   SYSTEM       *
*                                           *
*********************************************


                         RUN NUMBER A-M-35
                          INTEGRATED RUN
                         DATE     6/26/1980


                    STREAM COMPOSITION (MOL %)
                    ------ -----------

        SOUR GAS   SWEETGAS   FLASHGAS   STRIPN2   ACID GAS   ABSORBOT*   FLASHBOT*   STRIPBOT*

CO2      28.010      0.950     42.450      0.000    71.900      5.674       5.361       0.000
H2S       0.807      0.037      0.526      0.000     1.970      0.162       0.159       0.008
COS       0.045      0.003      0.038      0.000     0.127      0.009       0.009       0.000
MEOH      0.000      0.000      1.310      0.000     2.910     93.934      94.365      99.901
H2       33.190     45.500      4.210      0.000     0.000      0.118       0.085       0.090
CO       20.200     27.850     23.830      0.000     1.630      0.048       0.000       0.000
N2       15.700     23.230     13.490    100.000    20.750      0.000       0.000       0.000
CH4       2.010      2.440      4.110      0.000     0.690      0.054       0.021       0.000


                    * CALCULATED


                    MASS BALANCE (LB-MOLES/HR)
                    ---- -------

                IN                       OUT
                --                       ---

        SOUR GAS   STRIP N2     SWEETGAS   FLASHGAS   ACID GAS     TOTAL IN*   TOTAL OUT*   % RECOVERY

CO2      0.618      0.000        0.015      0.036      0.582        0.618       0.633         102.4
H2S      0.018      0.000        0.001      0.000      0.016        0.018       0.017          95.3
COS      0.001      0.000        0.000      0.000      0.001        0.001       0.001         111.9
MEOH     0.000      0.000        0.000      0.001      0.024        0.000       0.000           0.0
H2       0.732      0.000        0.719      0.004      0.000        0.732       0.723          98.8
CO       0.445      0.000        0.440      0.020      0.013        0.445       0.474         106.3
N2       0.346      0.182        0.367      0.011      0.168        0.528       0.547         103.4
CH4      0.044      0.000        0.039      0.003      0.006        0.044       0.048         107.5

TOTAL    2.205      0.182        1.581      0.085      0.809        2.386       2.441         102.301
(LB-MOLES/HR)


                    * METHANOL-FREE BASIS


        TOTAL METHANOL LOSS=  0.025 LB-MOLES/HR =  0.117 GALLONS/HR
```

```
                                   RUN NUMBER A-M-35
                                    INTEGRATED RUN
                                   DATE    6/26/1980



                        COLUMN TEMPERATURE PROFILES & MASS BALANCES
                        ------ ----------- -------- - ---- --------


            ABSORBER                   FLASH TANK                STRIPPER

            P=396.61 PSIG              P= 96.75 PSIG             P=  9.87 PSIG


              .---> SWEET                .---> FLASH               .---> ACID
              :     GAS                  :     GAS                 :     GAS
              :                          :                         :
              :                          :                         :
            9.46 SCFM                  0.51 SCFM                 4.84 SCFM
            (70.65 F)                  (82.49 F)                 (71.32 F)
              :                          :                         :
            ##########                   :                       ##########
            #        #                   :                       #        #
  NEOH FLOW #        #                   :           .-- 0.79 GPM -#        #
--- 0.79 GPM -->#    #                   :           :  (33.06 F) #        #
 (-36.31  F) #       #                   :           :            #        #
            #        #                ##########     :            # 13.65 F#
            # XXXXXX #                #        #     :            # 17.31 F#
            # XXXXXX #                #        #     :            #        #   DP= 0.48 IN H20
DP= 2.50 IN H20      #                # 9.51 F #     :            #        #
            #        #                #        #     :            # 11.05 F#
            # XXXXXX #                #        #     :            # 16.13 F#
            # XXXXXX #        .------->#       #     :            #        #
            #        #        :       #        #     :            #        #
            #-34.05 F#        :       #        #-----'            # 16.08 F#
            #-34.65 F#        :       #        #---------->       # 16.12 F#
            #        #        :       ##########                  #        #
  SOUR GAS  #        #        :                                   #        #
-- 13.19 SCFM -->#   #        :   STRIPPING H2-- 1.09 SCFM -->#   #        #
  ( 53.86 F) #       #        :                    (75.00 F)      # 33.15 F#
            #  0.72 F#        :                                   #        #--TO ABSORBER-->
            #        #------------->                              #        #
            #        #                                            #        #
            ##########                                            ##########
```

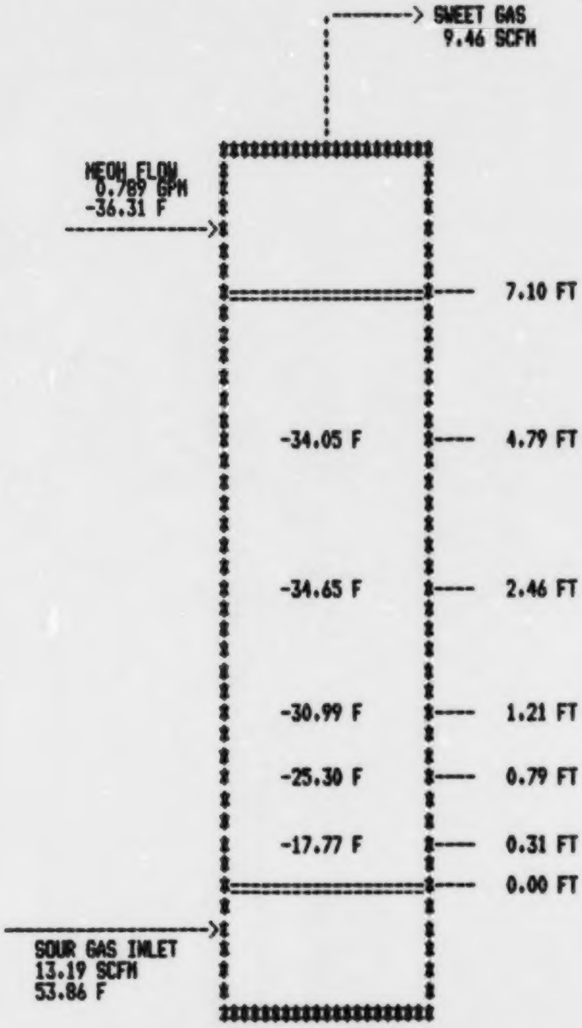
```
                    RUN NUMBER A-M-35
                     INTEGRATED RUN
                    DATE    6/26/1980

                COLUMN TEMPERATURE PROFILE
                ------ ----------- -------

          ABSORBER COLUMN PRESSURE =396.6 PSIG

          TOTAL PACKING HEIGHT= 7.10 FEET

          PACKING USED = 1/4" CERAMIC INTALOX SADDLES
```


SWEET GAS
9.46 SCFM
MEOH FLOW
0.789 GPM
-36.31 F
7.10 FT
-34.05 F
4.79 FT
-34.65 F
2.46 FT
-30.99 F
1.21 FT
-25.30 F
0.79 FT
-17.77 F
0.31 FT
0.00 FT
SOUR GAS INLET
13.19 SCFM
53.86 F

```
 TRANSMITTER      HEIGHT ABOVE      HEIGHT OF      TEMPERATURE(F)
                   GAS INLET         PACKING

 TT350               4.79              4.79            -34.05
 TT351               2.46              2.46            -34.65
 TT352               1.21              1.21            -30.99
 TT353               0.31              0.31            -17.77
 TT354               0.79              0.79            -25.30
```

AM-36

```
**********************************************
*                                            *
* NCSU DEPARTMENT OF CHEMICAL ENGINEERING    *
*                                            *
*        ACID   GAS   REMOVAL   SYSTEM       *
*                                            *
**********************************************


                       RUN NUMBER A-M-36
                        INTEGRATED RUN
                       DATE    7/18/1980



                    STREAM COMPOSITION (MOL %)
                    ------ -----------

                                                                    *          *          *
         SOUR GAS   SWEETGAS   FLASHGAS   STRIPN2    ACID GAS   ABSORBOT   FLASHBOT   STRIPBOT

CO2       20.900      0.420     34.170      0.000     69.770      4.465      4.302      0.000
H2S        0.892      0.068      0.569      0.000      2.225      0.182      0.180      0.023
COS        0.048      0.004      0.038      0.000      0.133      0.010      0.010      0.000
MEOH       0.000      0.000      0.000      0.000      0.000     95.037     95.411     99.947
H2        33.440     44.310     13.870      0.000      0.000      0.000      0.000      0.000
CO        17.030     20.580     22.020      0.000      0.970      0.214      0.098      0.030
N2        26.190     33.040     26.490    100.000     26.500      0.093      0.000      0.000
CH4        1.270      1.680      2.830      0.000      0.360      0.000      0.000      0.000


                   *
                    CALCULATED



                   MASS BALANCE (LB-MOLES/HR)
                   ---- -------


                IN                          OUT
                --                          ---

                                                                       *            *
         SOUR GAS   STRIP N2      SWEETGAS   FLASHGAS   ACID GAS      TOTAL IN   TOTAL OUT   % RECOVERY

CO2        0.476      0.000         0.007      0.019      0.518         0.476      0.545        114.4
H2S        0.020      0.000         0.001      0.000      0.017         0.020      0.018         88.9
COS        0.001      0.000         0.000      0.000      0.001         0.001      0.001         99.3
MEOH       0.000      0.000         0.000      0.000      0.000         0.000      0.000          0.0
H2         0.762      0.000         0.787      0.008      0.000         0.762      0.795        104.3
CO         0.388      0.000         0.366      0.012      0.007         0.388      0.385         99.2
N2         0.597      0.182         0.587      0.015      0.197         0.779      0.798        102.5
CH4        0.029      0.000         0.030      0.002      0.003         0.029      0.034        117.8

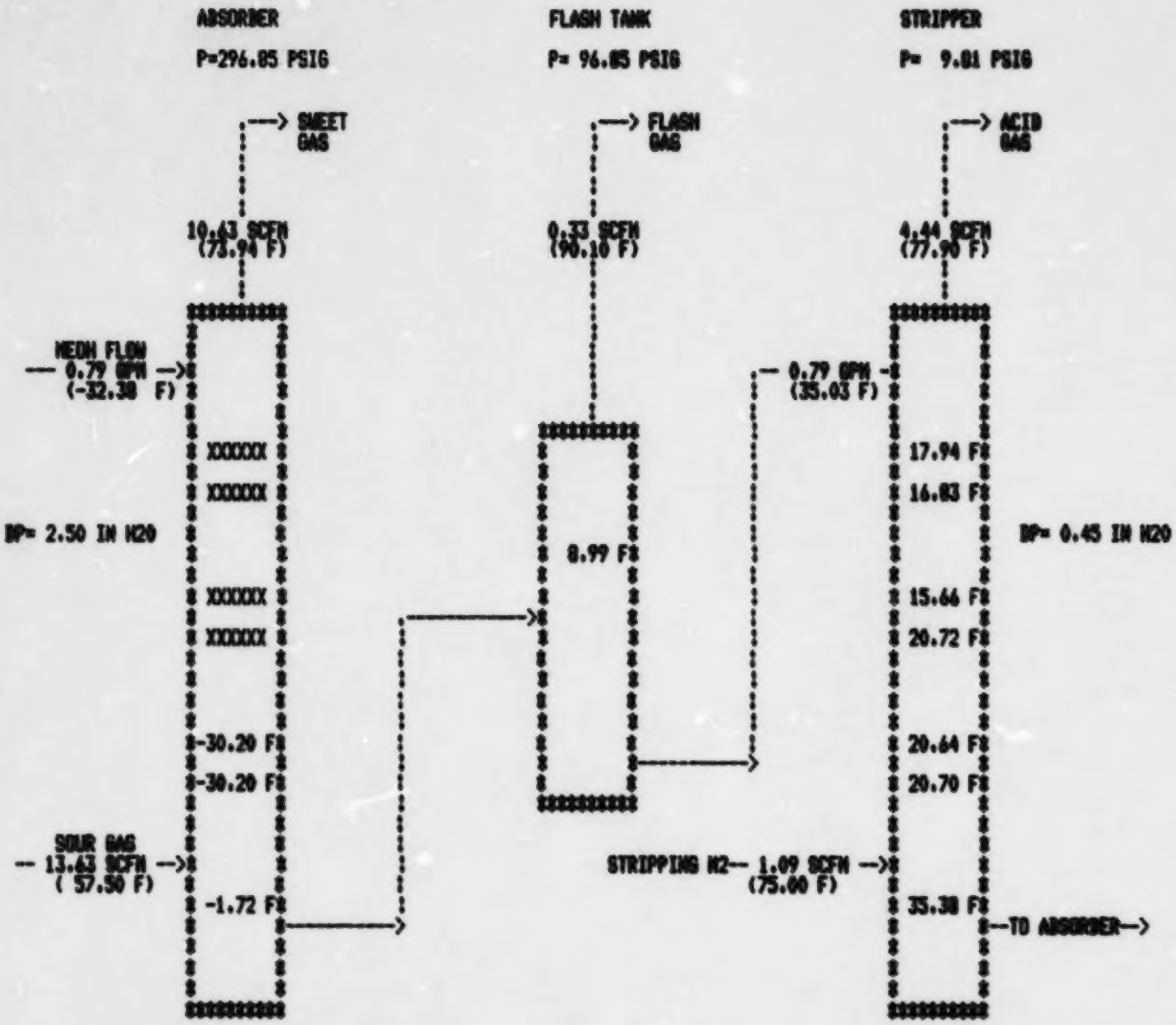
TOTAL      2.278      0.182         1.776      0.055      0.743         2.455      2.576        104.918
(LB-MOLES/HR)


                   *
                    METHANOL-FREE BASIS


           TOTAL METHANOL LOSS=  0.000 LB-MOLES/HR =  0.000 GALLONS/HR
```

RUN NUMBER A-K-36
INTEGRATED RUN
DATE 7/18/1980

COLUMN TEMPERATURE PROFILES & MASS BALANCES


ABSORBER
P=296.05 PSIG
FLASH TANK
P= 96.05 PSIG
STRIPPER
P= 9.01 PSIG
SWEET GAS
FLASH GAS
ACID GAS
10.43 SCFM
(73.94 F)
0.33 SCFM
(90.10 F)
4.44 SCFM
(77.90 F)
MEOH FLOW
0.79 GPM
(-32.38 F)
0.79 GPM
(35.03 F)
XXXXXX
XXXXXX
XXXXXX
XXXXXX
DP= 2.50 IN H20
8.99 F
17.94 F
16.83 F
DP= 0.45 IN H20
15.66 F
20.72 F
-30.20 F
-30.20 F
20.64 F
20.70 F
SOUR GAS
13.63 SCFM
(57.50 F)
STRIPPING N2 1.09 SCFM
(75.00 F)
-1.72 F
35.38 F
TO ABSORBER

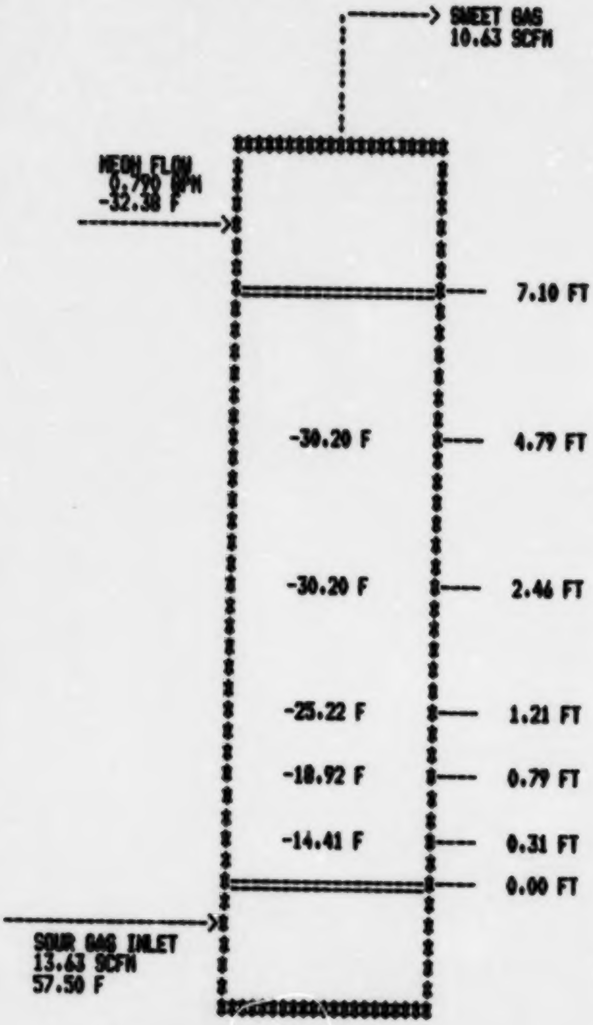
RUN NUMBER A-M-36
INTEGRATED RUN
DATE 7/18/1980

COLUMN TEMPERATURE PROFILE

ABSORBER COLUMN PRESSURE =296.9 PSIG

TOTAL PACKING HEIGHT= 7.10 FEET

PACKING USED = 1/4" CERAMIC INTALOX SADDLES


SWEET GAS
10.63 SCFM
MEOH FLOW
0.790 GPM
-32.38 F
7.10 FT
-30.20 F
4.79 FT
-30.20 F
2.46 FT
-25.22 F
1.21 FT
-18.92 F
0.79 FT
-14.41 F
0.31 FT
0.00 FT
SOUR GAS INLET
13.63 SCFM
57.50 F

TRANSMITTER	HEIGHT ABOVE GAS INLET	HEIGHT OF PACKING	TEMPERATURE(F)
TT350	4.79	4.79	-30.20
TT351	2.46	2.46	-30.20
TT352	1.21	1.21	-25.22
TT353	0.31	0.31	-14.41
TT354	0.79	0.79	-18.92

AM-37

```
                  ***************************************
                  *                                     *
                  * NCSU DEPARTMENT OF CHEMICAL ENGINEERING *
                  *                                     *
                  *      ACID   GAS   REMOVAL   SYSTEM   *
                  *                                     *
                  ***************************************


                            RUN NUMBER A-M-37
                             INTEGRATED RUN
                            DATE    7/25/1980



                        STREAM COMPOSITION (MOL %)
                        ------ -----------

                                                                        *          *          *
        SOUR GAS   SWEETGAS   FLASHGAS   STRIPN2    ACID GAS   ABSORBOT   FLASHBOT   STRIPBOT

CO2      25.050      0.640     47.820      0.000     71.050      5.406      4.975      0.000
H2S       0.863      0.041      0.628      0.000      2.260      0.183      0.179      0.000
COS       0.047      0.003      0.043      0.000      0.130      0.010      0.010      0.000
MEOH      0.000      0.000      0.870      0.000      4.030     93.853     94.667     99.850
H2       38.930     54.960     11.880      0.000      0.000      0.000      0.000      0.000
CO       18.810     23.920     22.340      0.000      0.940      0.310      0.089      0.015
N2       14.820     19.300     12.940    100.000     21.150      0.171      0.044      0.114
CH4       1.150      1.160      3.140      0.000      0.220      0.067      0.037      0.020


                       *
                        CALCULATED



                        MASS BALANCE (LB-MOLES/HR)
                        ---- -------


              IN                         OUT
              --                         ---

                                                                       *           *
        SOUR GAS   STRIP N2      SWEETGAS   FLASHGAS   ACID GAS      TOTAL IN   TOTAL OUT   % RECOVERY

CO2      0.579      0.000         0.011      0.050      0.589         0.579      0.650        112.2
H2S      0.020      0.000         0.001      0.001      0.019         0.020      0.020        100.6
COS      0.001      0.000         0.000      0.000      0.001         0.001      0.001        106.6
MEOH     0.000      0.000         0.000      0.001      0.033         0.000      0.000          0.0
H2       0.900      0.000         0.525      0.012      0.000         0.900      0.937        104.1
CO       0.435      0.000         0.402      0.023      0.008         0.435      0.434         99.7
N2       0.343      0.182         0.325      0.013      0.175         0.525      0.514         97.9
CH4      0.027      0.000         0.020      0.003      0.002         0.027      0.025         92.5

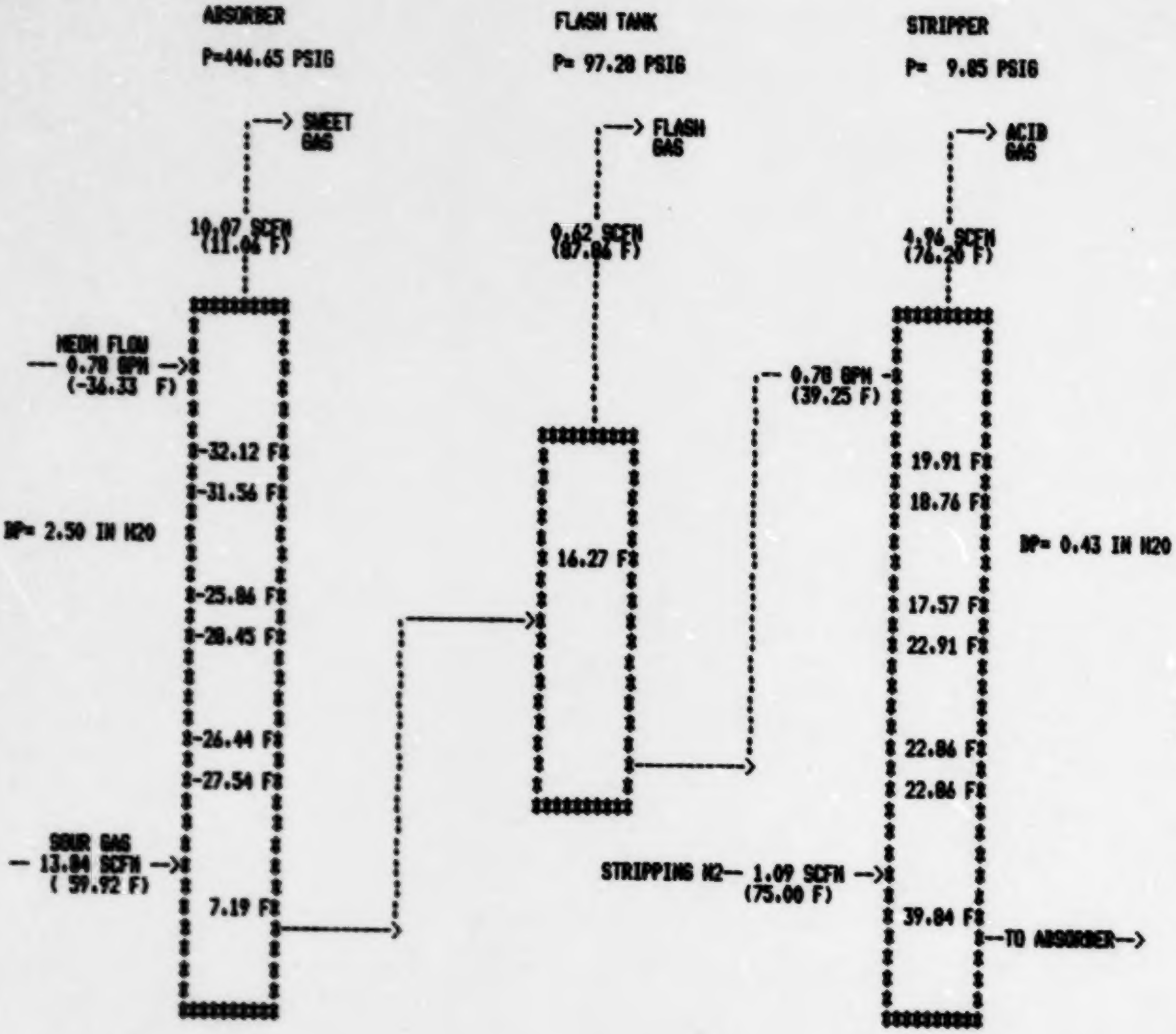
TOTAL    2.313      0.182         1.683      0.104      0.830         2.487      2.580        103.732
(LB-MOLES/HR)


                       *
                        METHANOL-FREE BASIS


        TOTAL METHANOL LOSS=  0.034 LB-MOLES/HR =  0.164 GALLONS/HR
```

RUN NUMBER A-H-37
INTEGRATED RUN
DATE 7/25/1980

COLUMN TEMPERATURE PROFILES & MASS BALANCES


ABSORBER
P=446.65 PSIG
FLASH TANK
P= 97.28 PSIG
STRIPPER
P= 9.85 PSIG
SWEET GAS
FLASH GAS
ACID GAS
10.07 SCFM (11.06 F)
0.62 SCFM (87.86 F)
4.96 SCFM (76.20 F)
MEOH FLOW 0.70 GPM (-36.33 F)
0.70 GPM (39.25 F)
-32.12 F
-31.56 F
DP= 2.50 IN H20
-25.86 F
-28.45 F
-26.44 F
-27.54 F
SOUR GAS 13.84 SCFM (59.92 F)
7.19 F
16.27 F
19.91 F
18.76 F
DP= 0.43 IN H20
17.57 F
22.91 F
22.86 F
22.86 F
STRIPPING N2 1.09 SCFM (75.00 F)
39.84 F
TO ABSORBER

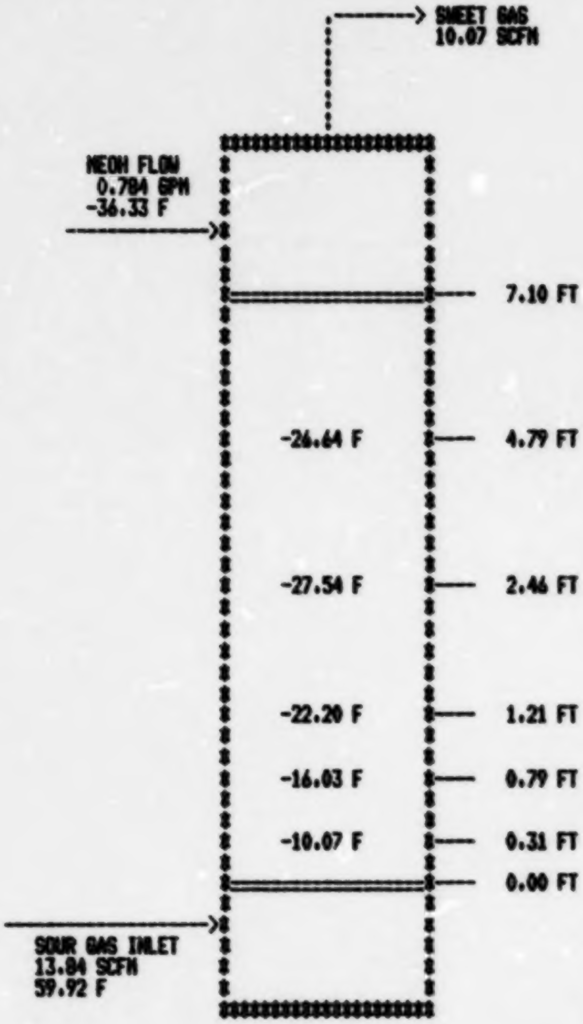
RUN NUMBER A-N-37
INTEGRATED RUN
DATE 7/25/1980

COLUMN TEMPERATURE PROFILE

ABSORBER COLUMN PRESSURE =446.6 PSIG

TOTAL PACKING HEIGHT= 7.10 FEET

PACKING USED = 1/4" CERAMIC INTALOX SADDLES


SWEET GAS
10.07 SCFM
MEOH FLOW
0.784 GPM
-36.33 F
7.10 FT
-26.64 F
4.79 FT
-27.54 F
2.46 FT
-22.20 F
1.21 FT
-16.03 F
0.79 FT
-10.07 F
0.31 FT
0.00 FT
SOUR GAS INLET
13.84 SCFM
59.92 F

TRANSMITTER	HEIGHT ABOVE GAS INLET	HEIGHT OF PACKING	TEMPERATURE(F)
TT350	4.79	4.79	-26.64
TT351	2.46	2.46	-27.54
TT352	1.21	1.21	-22.20
TT353	0.31	0.31	-10.07
TT354	0.79	0.79	-16.03

POLLUTION CONTROL GUIDANCE DOCUMENT
FOR
LOW-BTU GASIFICATION TECHNOLOGY:

BACKGROUND STUDIES

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ABSTRACT

The Environmental Protection Agency is currently preparing a Pollution Control Guidance Document (PCGD) for low-Btu gasification (LBG) facilities which use atmospheric pressure, fixed-bed gasifiers. The PCGD is intended to aid industry and government in their efforts to commercialize LBG technology in an environmentally acceptable manner. This paper presents some of the preliminary results of background studies performed to support the development of the LBG PCGD.

A model plant approach was used to assess the environmental control needs for LBG facilities. The plant configuration and coal feed combinations for which pollution controls were identified and evaluated were selected based on existing and proposed plants in the U.S. The major variables examined were coal feed type (anthracite, lignite, and high- and low-sulfur bituminous coals) and degree of product gas purification (production of hot, cooled, and desulfurized low-Btu gas). In all, eleven combinations of these variables, i.e., model plants, were selected for study. Each model plant had a nominal capacity of 45 MJ/s (150 x 10^6 Btu/hr) of low-Btu gas.

Multimedia pollutant sources and pollutants of potential concern were identified and quantified for each model plant. The bases for these determinations were field test data and calculated emissions projections. The EPA's low-Btu gasification environmental assessment program was the major source of the field test data, but results from other government and industry test programs were also used.

Control/disposal options were identified and evaluated for each discharge stream. Factors that were considered included the need for control, current industry practices, control equipment performance, capital investment requirements, annual operating costs, energy impacts, and secondary environmental discharges.

POLLUTION CONTROL GUIDANCE DOCUMENT
for
LOW-BTU GASIFICATION TECHNOLOGY:

BACKGROUND STUDIES

INTRODUCTION

Over the past several years the United States has moved from a position of energy independence to one of energy dependence. A decade ago this country imported only about ten percent of its crude oil needs and now the figure is around fifty percent. The amount of oil and gas produced in the U.S. has declined slightly over this period despite a doubling of drilling activity. The country's vast coal reserves, however, have not been developed with the same intensity. With the changing energy picture there has been a growing interest on the part of government and industry in the technologies that produce clean fuels and chemical feedstocks from coal. One such technology is low-Btu coal gasification (LBG).

The Environmental Protection Agency is responsible for ensuring that LBG technology and other alternate energy technologies are developed in a manner which protects public health and the environment. As part of that effort, the EPA has initiated programs to assess the environmental impacts of LBG.

The EPA has developed the Pollution Control Guidance Document (PCGD) concept to aid industry and government in their efforts to commercialize low-Btu gasification technology in a manner that will be environmentally acceptable. The primary purposes of a PCGD are to:

- Provide guidance to permit writers on the best control approaches presently available at a reasonable cost for the processes under consideration.
- Provide system developers with an early indication of EPA's assessment of the appropriate multimedia environmental protection needs for each of these processes, considering costs, so that developers can design their facilities to achieve this level of protection (rather than add potentially more costly retrofit controls later).
- Describe to public interest groups EPA's judgment of the best available controls for these processes.
- Provide the regulatory offices in EPA with information useful in developing future regulations.

The low-Btu gasification PCGD will describe the performance capabilities and costs of currently available controls for LBG facilities which use fixed-bed, atmospheric pressure gasifiers. (This type of gasifier is believed to be the likely candidate for near-term commercial use). The PCGD will provide guidance both for currently regulated pollutants and for sources and/or pollutants not covered by current standards. The guidance will be based on a coordinated evaluation of available data by EPA's research and development, regulatory, and permitting/enforcement offices. In the PCGD, suggested levels of environmental protection considering costs, multimedia tradeoffs, and control system reliability will be specified for all air, water, solid waste, and product/by-product streams. The PCGD will consist of three volumes whose contents can be summarized as follows:

- Volume I will describe the technology, identify applicable existing regulations, and present the control guidance;
- Volume II will summarize all of the data employed and present the baseline engineering design, waste stream characterizations and control option evaluations; and
- Volume III (Appendices) will contain detailed data listings and calculations which support the guidance.

This paper presents some of the preliminary results of background studies being conducted to support the development of the LBG PCGD. Included in this paper are: 1) a description of the technology and an identification and characterization of its multimedia discharges (including flow rates and factors affecting discharge characteristics); 2) an identification and evaluation of available control techniques; and 3) an estimation of the capital and annualized cost impacts of available controls.

Technology Overview

Low-Btu coal gasification technology has been commercially available for over 60 years. In the U.S., there are currently 20 known LBG plants either in operation, under construction, or being planned for construction in the near future. All of the commercially operating plants use fixed-bed, atmospheric pressure gasifiers and are generally located in the industrialized Midwest and Northeast regions of the Country. Feedstocks used at those plants include anthracite, lignite, and low-sulfur (<1%) bituminous coal. No high-sulfur coals are currently in use. The only gas purification process used at most of these plants is a hot gas cyclone for particulate removal. Tar and oil removal using gas quenching/scrubbing is practiced at one plant and is proposed for several future plants. Sulfur compound removal is currently practiced only at one plant. Current end-uses of low-Btu product gas include fuel for brick and lime kilns, process heaters, and steam boilers.

LBG systems featuring fixed-bed, atmospheric pressure gasifiers are most suitable for relatively small applications, with fuel demands ranging from about 8.8 to 88 MW of thermal energy (30-300 million Btu/hr). This would require using from 1 to 10 gasifiers, depending on the coal feed. Energy demands greater than about 88 MW (300 million Btu/hr) may be better served by gasification systems using gasifiers with larger capacities (for example, pressurized gasifiers).

Applicable Existing Federal Regulations

New low-Btu gasification plants will have to comply with existing Federal regulations for 1) sources within the plant that are already subject to regulation (NSPS); 2) the disposal of solid wastes (RCRA); and 3) ambient-based limitations, such as National Ambient Air Quality Standards (NAAQS), Prevention of Significant Deterioration (PSD) requirements, Water Quality Criteria, and Drinking Water Standards which may indirectly limit the quantities or concentrations of compounds in specific source discharges. However, at the current time there are no Federal regulations which apply to specific air or water discharge sources within an LBG facility. In addition, products and by-products may be subject to restrictions if they contain toxic substances.

New plants will also be required to comply with state and local regulations. The guidance in the PCGD is not intended to supersede the requirements of any of these existing or proposed regulations.

Approach Used For Background Studies

In conducting the background studies, an inventory of waste streams and pollutants generated in model plant facilities was prepared and an assessment of the performance and costs of various control alternatives for those streams and pollutants was made. The approaches used to develop the pollutant inventory and to select and evaluate applicable controls are briefly described below.

Pollutants Considered. A listing of all the currently regulated pollutants which have been found in the gaseous and aqueous wastes from LBG facilities is provided in Table 1. The major pollutants not listed in this table, but which are expected to be present in an LBG system's discharges are polycyclic organic matter (POM), hydrogen cyanide and ammonia in the uncontrolled gaseous emissions, and a number of specific organic compounds which are only covered by gross parameters such as "organic carbon" in the aqueous effluents.

Model Plants. A model plant approach was used to characterize the potential uncontrolled discharges from LBG systems and to evaluate pollution control alternatives for those discharges. The model plants selected represent processing configurations currently in use or proposed for use in the U.S. Each has similar processes in the coal preparation and coal gasification operations. They differ in the areas of coal feedstock used and the degree to which the low-Btu product gas is purified. For the background studies, recommendations were *not* made as to which model plant should be used, but pollution control information for the discharges from each model plant was developed.

TABLE 1. CONSTITUENTS IN LOW-BTU GASIFICATION PLANT WASTE STREAMS COVERED BY EXISTING AIR AND WATER STANDARDS

Standard	Subject Pollutants Found in Discharge Streams from Low-Btu Gasification Facilities
National Ambient Air Quality Standards	CO, NO_2, SO_2, Pb, TSP, NMHC
New Source Performance Standards	CO, NO_2, SO_2, TSP, Total Reduced Sulfur, NMHC
National Emission Standards for Hazardous Air Pollutants	Hg, Be, Inorganic As*, Benzene*, Radionuclides*
Prevention of Significant Deterioration Standards	
Increments	SO_2, TSP
De Minimis Levels	CO, NO_2, TSP, SO_2, Pb, Hg, Se, H_2S, CS_2, COS
Effluent Limitation Guidelines	
Conventional and nonconventional pollutants	Al, Ammonia, B, Ca, Fluoride, Fe, Mn, Nitrate, Organic Carbon, P, Sulfate, Sulfide, U, BOD_5, COD, pH, Total Nitrogen, Total Suspended Solids, Color, Oil and Grease, Settleable Solids
Consent decree pollutants (toxic pollutants)	Sb, As, Be, Cd, Cr, Cu, Cyanides, Pb, Hg, Ni, Phenol and phenolic compounds, Polynculear aromatic hydrocarbons, Se, Ag, Zn

*Listed as hazardous air pollutants; no regulations promulgated.

The characteristics of the coal being gasified influence the presence, composition and flow rates of the discharges from low-Btu gasification plants. In order to evaluate the impact of coal properties on the discharge streams, four different coals were examined: anthracite, lignite, low-sulfur bituminous coal, and high-sulfur bituminous coal. These feedstocks span the range of coals and coal properties which are or might be used in low-Btu gasification plants.

Using the data sources described below, mass balances were calculated for a basic plant capacity of 45 MW (approximately 150 x 10^6 Btu/hr) of thermal energy in the product gas (based on the higher heating value of the gas). This capacity is representative of the plant sizes expected to be constructed in the near future. The mass balances provided a consistent basis for calculating "uncontrolled" mass discharge rates.

Based upon the expected characteristics of the waste streams, pollution control processes were identified and evaluated. "Secondary" waste streams resulting from pollution control were also defined and controls for these streams evaluated.

Data Sources. The major source of data used in the background studies is an EPA-sponsored environmental assessment program for low-Btu gasification technology. As part of that program, a series of field test programs are being conducted. To date, three data acquisition programs have been completed, another is on-going and a fifth is planned for the fall of 1980.[1,2,3] All test sites are either commercially operating or commercial-size demonstration units located in the U.S. Additional data sources are other government and industry sponsored test programs.

Information used to identify and evaluate pollution control alternatives was mainly obtained by technology transfer, i.e., extrapolation from other industries with identical or similar pollution control problems. Additional technical information was obtained from process vendors, process developers, and published literature. Only limited pollution control information was obtained from the field test programs because of the essentially "uncontrolled" nature of the sites tested.

PROCESS DESCRIPTION AND POLLUTANT SOURCES

Low-Btu coal gasification systems can be considered to consist of three basic operations: coal preparation, coal gasification, and gas purification. Each of these operations in turn consists of process modules that are employed to satisfy the functions of the operations.

As mentioned previously, a model plant approach was used to characterize the potential uncontrolled discharges from LBG systems and to evaluate pollution control alternatives for those discharges. Block diagrams of the three model plants examined are shown in Figure 1. These represent all the processing configurations of plants currently operating or proposed in the U.S.

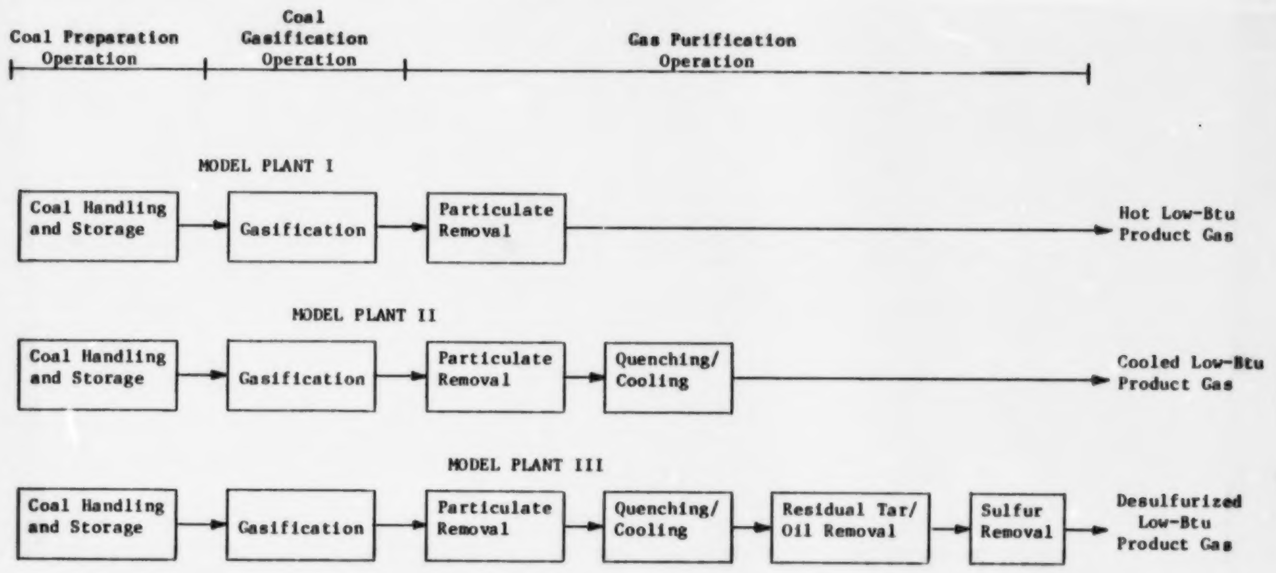
Coal Preparation Operation
Coal Gasification Operation
Gas Purification Operation
MODEL PLANT I
Coal Handling and Storage
Gasification
Particulate Removal
Hot Low-Btu Product Gas
MODEL PLANT II
Coal Handling and Storage
Gasification
Particulate Removal
Quenching/ Cooling
Cooled Low-Btu Product Gas
MODEL PLANT III
Coal Handling and Storage
Gasification
Particulate Removal
Quenching/ Cooling
Residual Tar/ Oil Removal
Sulfur Removal
Desulfurized Low-Btu Product Gas

FIGURE 1. LOW-BTU GASIFICATION MODEL PLANTS

The first model plant produces a hot low-Btu product gas. The only gas purification process used is a hot gas cyclone for partial removal of entrained particulate matter. This process configuration is typical of most of the plants currently in operation and several plants which are proposed or under construction.

The second model plant produces a cooled low-Btu product gas. In this plant, a series of wet scrubbers are used to quench and cool the hot gas. This step also removes additional particulate matter and the majority of tars and oils present. This configuration is similar to an existing LBG plant which uses Chapman gasifiers.

The third model plant produces a desulfurized product gas and as a result has the most extensive gas purification scheme. In addition to a hot gas cyclone and quenching/cooling, this model plant uses an electrostatic precipitator for removal of residual tars/oils and a sulfur removal process. Available sulfur removal processes can be broadly classified as 1) those that remove sulfur compounds and directly convert them into elemental sulfur, and 2) those that remove sulfur compounds and produce an off-gas containing the removed sulfur species. An evaluation of these processes, including discussions with process licensors, indicated that the direct oxidation processes are the preferred sulfur removal technique for low-Btu gas derived from fixed-bed, atmospheric pressure gasifiers. While some of the other types of processes (e.g., the monoethanolamine process) could be used, difficulties would be encountered in treating the sulfur species laden off-gas due to its high CO_2 content. This conclusion is supported by the fact that all existing and proposed designs of LBG facilities which remove sulfur species use direct oxidation processes. Thus, for the Model Plant III systems, only direct oxidation processes are examined for sulfur removal. For study purposes, the Stretford process was selected as being representative of commercially available direct oxidation processes.

Descriptions of the three basic operations, the process modules which might be found in them, and the potential discharges from each operation are presented in the following sections.

Description Of The Coal Preparation Operation

Fixed-bed, atmospheric pressure gasifiers require a sized coal feed. Current practice at all commercial LBG facilities in the U.S. is to purchase pre-sized coal, eliminating the need for on-site crushing and sizing equipment. Future LBG facilities are also expected to purchase pre-sized coal. As a result, coal preparation requirements for these facilities will most likely consist only of coal receiving and storage, and means for transporting coal from storage to the gasifier coal feed hoppers. Some facilities though may have to perform final, on-site sizing if fuel size degradation occurs in shipment.

Discharges from the coal preparation operation include airborne coal dust particles from coal handling, rainwater runoff from coal storage piles, and, if final on-site sizing is performed, small amounts of coal fines. No test data are available on the discharges from the coal preparation operation.

However, their physical and chemical characteristics can be estimated from data for similar discharges from the coal mining and coal-fired steam electric industries. Coal pile runoff tends to contain high levels of suspended and dissolved solids (including heavy metals) and can have an acidic or alkaline pH. Dissolved organics tend to be at negligible or non-detectable levels. Dust from coal handling and storage consists of small coal particles.

Description Of The Coal Gasification Operation

There are six commercially available gasifiers that operate in a fixed-bed mode and at atmospheric pressure. They are:

- Chapman (Wilputte),
- Foster-Wheeler/Stoic,
- Riley,
- Wellman-Galusha,
- Wellman Incandescent, and
- Woodall-Duckham/Gas Integrale.

These gasifiers produce low-Btu gas by countercurrent gasification of coal with a mixture of air and steam.

Coal is fed to the top of the gasifier from an overhead bin through a lock hopper and/or a rotary feeder. As the coal gravitates downward through the gasifier, it is contacted by rising hot gases and passes through "zones" of progressively higher temperatures before exiting the bottom of the gasifier as ash. As the coal is heated, it undergoes a series of physical and chemical reactions. Sequentially, these are drying, devolatilization, gasification, and finally combustion. Air saturated with water, i.e., steam, enters at the bottom of the gasifier. The steam absorbs some of the heat released in the combustion zone, which helps to maintain the combustion temperature below the coal ash softening temperature.

With most gasifiers, ash is collected at the bottom of the gasifier in a water sealed ash pan and removed from the unit using an ash plow. The Wellman-Galusha gasifier however, collects the ash in an ash hopper located beneath the gasifier. Ash is removed by adding water to the hopper and draining the ash slurry through a slide valve. The water also serves to seal the gasifier internals from the atmosphere during the ash removal step.

Pokeholes are located on the top of the gasifier. Rods are inserted through the pokeholes to measure the depth and location of the "fire" and ash zones. These rods can also be used to break up any agglomerates formed in the bed.

The Wellman-Galusha, Chapman, and Riley gasifiers produce a single low-Btu gas stream that exits the top of the gasifier. The Foster-Wheeler/Stoic, Wellman Incandescent, and Woodall-Duckham/Gas Integrale gasifiers are two-stage gasifiers that produce two gas streams. A "clear" gas stream, constituting approximately one-half of the total gas production, is withdrawn from the gasification zone (near the middle of the gasifier). As such, it contains essentially no tars or oils. The remaining gas, which contains tars and oils, is withdrawn from the top of the gasifier where devolatilization of the coal occurs.

At present, very limited environmental characterization data are available for two-stage gasification systems. From a process viewpoint, the two-stage gasification arrangement simplifies the gas purification operation, but it does not appear to alter materially the system's potential environmental impacts. The background study deals specifically with single-stage gasification systems. However, the information developed is felt to also be generally applicable to two-stage gasification systems.

Discharges from the coal gasification operation include:

- Gaseous emissions - pokehole gases
  - coal feeder gases
  - transient gases
- Liquid effluents - ash sluice water (from Wellman-Galusha gasifiers only)
- Solid wastes - gasifier ash

Coal feeder gases, pokehole gases, and transient gases generated during start-up, shutdown, and upset conditions are essentially raw low-Btu gas. These discharges contain primarily carbon monoxide, carbon dioxide, hydrogen, nitrogen, and water vapor. Minor components include hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, entrained particulates, trace elements, low molecular weight hydrocarbons, and, if the coal feed is lignite, bituminous, or subbituminous, higher molecular weight organics (e.g., tars and oils).

Ash sluice water from Wellman-Galusha gasifiers contains suspended and dissolved solids, including trace elements. Negligible or nondetectable levels of organics have been identified, with most of them being attributable to artifacts of the sampling and analytical procedures. The pH of ash sluice water can vary widely, depending on the characteristics of the ash. An alkaline pH is typical if lignite is the coal feed, while acidic or neutral pH's are typical for other coal feeds.

Ash from the gasifier is similar to bottom ash from a coal-fired boiler although higher levels of residual carbon are present. Data for gasification of several coals indicate that trace elements are not leachable in amounts which would result in classification of gasifier ash as a hazardous waste.

Description Of The Gas Purification Operation

The purpose of the gas purification operation is to remove undesirable constituents such as entrained particulate matter, tars, oils, and sulfur from the raw low-Btu gas. Depending on the concentrations of these constituents in the raw gas and on the product gas specifications imposed by the end-use (by either process or environmental considerations), none, some, or all of these constituents may need to be controlled. No attempt was made to evaluate systems producing a predefined product gas quality. Instead, systems were selected based on existing or proposed purification configurations, with the assumption that the resulting product gas quality would be sufficient to meet the user's needs.

Particulate Removal. Entrained particulate matter can be removed from the low-Btu gas with cyclones, wet scrubbers, and/or electrostatic precipitators (ESP). Cyclones are currently used in all domestic commercial LBG facilities.

Tars and Oils Removal. The primary means of removing tars and oils from raw low-Btu gas is to use wet scrubbers. These include in-line sprays, wet cyclones, and spray, tray, or packed scrubbers. Most of the commercially available sulfur removal processes have limitations on the concentrations of tars and oils in the gas to be treated. Normally, these levels cannot be achieved using wet scrubbers alone. Detarrers (electrostatic precipitators) have been used with some success for residual tars and oils removal.

Tars/oils-laden water from the scrubbers is directed to a gravity separator. Here, the heavier-than-water tars/oils are separated from the water and recovered as a by-product. The scrubber water is then cooled in indirect heat exchangers and recycled. Some volatile organic and inorganic species are absorbed from the low-Btu gas when it is scrubbed. These species tend to desorb from the scrubber water and fill the separator vapor space. They can be recombined with the low-Btu gas by ducting the vapor space to the low-Btu gas line.

In order to control the buildup of dissolved solids in the recirculating scrubber water and/or to maintain a water balance in the scrubbing loop, a portion of the scrubber water is removed as blowdown. The size of this blowdown depends on such factors as the moisture and chloride content of the coal, the dew point of the hot low-Btu gas and the temperature to which the gas is cooled.

Sulfur Compounds Removal. Commercially available sulfur removal processes include those using physical solvents, chemical solvents, combinations of physical and chemical solvents, and processes featuring removal and direct oxidation of sulfur compounds to produce elemental sulfur.[4] Physical solvent, combination chemical and physical solvents and some of the chemical solvent processes are not well suited to the removal of sulfur compounds from an atmospheric pressure, low-Btu gas.[5] Several of the alkanolamine (chemical solvent) processes can be used, but they require moderate pressurization of the gas in order to obtain low residual sulfur levels. Regeneration of the alkanolamine solvent also produces an off-gas which contains the removed H_2S and CO_2, and which must be further processed for sulfur recovery. Standard means of treating these off-gases (which will contain 70-95% CO_2) is to route them to a Claus unit. The low H_2S/high CO_2 content of these off-gases can limit the recovery efficiency of the Claus unit and prohibit the use of a Claus tail gas treatment process such as the SCOT unit. Thus, while alkanolamine processes appear to be feasible for treating low-Btu gas, technical (and economic) considerations indicate they are a poor choice. In light of the above factors, none of the chemical or physical solvent processes were evaluated in the background studies for the model plant III configurations.

The direct oxidation processes do not have gas pressure limitations and are very effective in removing H_2S. These processes also convert the removed H_2S directly into elemental sulfur, thus eliminating the need for additional treatment of an H_2S-laden off-gas. However, direct oxidation processes do not remove significant amounts of non-H_2S sulfur species such as carbonyl sulfide (COS).[5] For purposes of analysis, the Stretford process was selected as a representative example of a commercially available direct oxidation type sulfur removal process.

Summary of Discharges from Gas Purification. The existence, quantity, and characteristics of discharges from the gas purification operation depend on the degree of gas purification desired. In general terms, as the low-Btu gas undergoes additional clean-up, additional waste streams are created. These waste streams include:

- collected particulate matter from cyclones (all Model Plants),
- scrubbing liquor blowdown (Model Plants II and III),
- by-product tars and oils (Model Plants II and III except for anthracite feed), and
- vent gas and sulfur cake from direct oxidation sulfur removal processes (Model Plant III).

Collected particulates or cyclone dust has a very high carbon content and resembles devolatilized coal. Leaching tests indicate that cyclone dust is not a toxic waste.

Scrubbing liquor blowdown contains suspended solids, dissolved inorganics (including trace elements and soluble gaseous components such as H_2S and NH_3), and, unless anthracite is the coal feed, dissolved organics. By-product tars/oils derived from gasification of non-anthracite coals are predominantly organic material, but also contain ash and various trace elements. This material has a significant energy content, and represents a fuel resource which should be recovered.

Discharges from the sulfur removal module include vent gases from the Stretford oxidizer and sulfur cake. The oxidizer gases contain primarily nitrogen, oxygen, and water vapor, with minor amounts of ammonia, carbon dioxide, and reduced sulfur compounds. Other components of the low-Btu gas may also be absorbed by the Stretford scrubbing liquor and released in the oxidizer. However, this is not expected to occur to any significant extent.

Sulfur produced in the Stretford process is initially recovered as a cake containing nominally 50% water. Dissolved in the water are Stretford scrubbing chemicals (sodium vanadates, anthraquinone disulfonic acid, ethylene diamine tetracetic acid, iron, carbonates, and bicarbonates) and high levels of nonregenerable sulfur components such as sulfates, thiosulfates, and thiocyanates.

EVALUATION OF POLLUTION CONTROL TECHNOLOGIES

Evaluations of control technologies for application to individual waste streams were based on considerations of control efficiency, ability to comply with emissions regulations, capital and operating costs, energy and resource consumption, reliability, simplicity, multi-pollutant abatement capability, residue generation and disposal requirements, potential for recovery of by-products, and stage of development. The above criteria were used as a basis for comparison of candidate control technologies either used alone or in combination with in-plant control methods or other add-on controls.

Performance data for applicable control technologies were obtained primarily from the open literature supplemented by vendor supplied data in some cases. The capabilities of various control technologies were not usually assessed on a design-specific basis but rather upon a generalized basis derived from test results and/or engineering studies of the subject technologies.

In many cases performance can only be estimated in terms of control of major constituents (e.g., carbon monoxide) or gross parameters (e.g., TOC) since often no information is available for removal efficiencies for specific substances. Further, even in those cases where substance-specific performance information exists for a control technology, accurate or complete characterization of the waste streams requiring control may be lacking. In the final analysis of course, the capabilities of state-of-the-art controls for LBG facilities can be accurately evaluated only by testing operating facilities. Since these opportunities are generally not available, the performance estimates presented here are believed to reflect the best information currently available based on actual experience and/or engineering analysis.

Air Pollution Control

The uncontrolled gaseous emissions from LBG facilities are summarized in Table 2. The pollutants of potential concern, factors affecting the emission characteristics, and estimated emission flow rates are also summarized in this table. Available control techniques for these emissions are discussed below.

TABLE 2. UNCONTROLLED ATMOSPHERIC EMISSIONS FROM LOW-BTU GASIFICATION FACILITIES

Uncontrolled Atmospheric Emissions	Pollutants of Potential Concern	Factors Affecting Emissions Characteristics	Estimated Flowrate of Uncontrolled Emissions
Airborne particulates from coal handling and storage (All Model Plants)	Particulates	Coal type; gasifier feed size requirements; type and condition of coal handling, crushing and sizing equipment	Not estimated, but believed to be negligible since presized coal is received at the plant site
Coal feeder gases (All Model Plants)	CO, H_2S, HCN, trace elements, and other low-Btu gas components	Coal feeder design and conditions; coal composition, feed rate and adsorption characteristics; system pressure	Anthracite: 56 m^3/hr (32 scfm) Low-sulfur bituminous: 53 m^3/hr (30 scfm) High-sulfur bituminous: 62 m^3/hr (35 scfm) Lignite: 110 m^3/hr (62 scfm)
Pokehole gases (All Model Plants)	CO, H_2S, HCN, trace elements, and other low-Btu gas components	Pokehole design and conditions; poking procedures and frequency; system pressure	Anthracite: 38 m^3/hr (22 scfm) Low-sulfur bituminous: 16 m^3/hr (9 scfm) High-sulfur bituminous: 16 m^3/hr (9 scfm) Lignite: 28 m^3/hr (16 scfm)
Stretford oxidizer vent gases (Model Plant III)	Reduced sulfur compounds, ammonia	Coal Composition; Stretford unit design and operation	Anthracite: 220 m^3/hr (130 scfm) Low-sulfur bituminous: 280 m^3/hr (160 scfm) High-sulfur bituminous: 2000 m^3/hr (1100 scfm) lignite: 600 m^3/hr (340 scfm)
Startup, shutdown and upset gases (All Model Plants)	CO, H_2S, HCN, trace elements, and other low-Btu gas components	Startup, shutdown and upset procedures; gasifier reliability	Not determined, highly variable

Note: m^3/hr flow is relative to 25°C and atmospheric pressure, scfm flow is relative to 60 °F and atmospheric pressure.

Airborne Particulates from Coal Handling and Preparation. Most LBG installations will receive coal that has been crushed and sized. For these installations, no significant particulate emissions are expected and therefore, no control is necessary. If the coal feed is crushed and sized on site, then airborne particulates generated by these operations may be a problem. Control techniques involve enclosing the coal unloading facility, storage bins, crushing and sizing equipment and any conveying devices. These enclosures should be vented by low pressure ducting to a central bag filter collection system. An induced draft fan at the outlet of the bag filters would provide the necessary air flow and ensure that any leakage would be into the system.

Coal Feeder Gases. Low-Btu gas can leak from the gasifier vessel through the coal feeder mechanism and up into the coal bin area by passing countercurrent to the coal flow. One method of reducing the hazards from this emission is to collect it before it enters the coal bin area and then disperse it to the atmosphere through a vent pipe. The top of the coal bin must be sealed (hooded) and a pipe run from there to an elevated outside venting point. An induced draft fan in the vent line would draw air into the coal bin through slots in the side of the bin. Coal feeder gases which pass up through the coal in the bin would then be swept into the vent pipe. While this control option incurs no significant operating costs or energy requirements, it does not decrease the amount of coal feeder gases emitted to the atmosphere.

Another, and more effective means of controlling these emissions is to return them to the process. This strategy can be done in one of two basic ways. One approach is to enclose the coal bin (as with the atmospheric venting option) and run a duct to the intake of the gasifier air blower. To provide continuous sweeping air in the coal bin (to prevent a possible explosive mixture in the bin during very low air rates), a small vent and blow-off valve will be needed in the air blower discharge line for venting during periods of low gasifier air requirements. A second approach involves slightly pressurizing the coal bin with an inert gas. This approach prevents the passage of low-Btu gases into the coal bin. Either of these control options can effect almost complete (99%) control of the coal feeder gases during normal gasifier operations.

Pokehole Gases. Low-Btu gas escapes from pokeholes during and between poking operations. Improved pokehole designs are available with closer tolerances and positive seal valves. While effective in reducing emissions between poking operations, this control method still allows significant quantities of gases to continue to escape during the poking operation.

A second control technology is to combine improved pokehole sealing methods with the injection of an inert gas during poking operations. The inert gas effectively eliminates low-Btu gas leakage. Nitrogen is a possible choice for the inert gas but this may incur operating costs (mainly for the purchase of nitrogen) of up to two percent of the base plant annualized costs. If available, steam might be a more economical choice since the steam requirement would be less than 0.1 percent of the product gas energy.

Stretford Oxidizer Vent Gases. For systems using the Stretford process to produce a desulfurized product gas, an air blown oxidizer is used to convert the reduced Stretford solution back to its oxidized form. A large excess of air is used in the oxidizer and released in the vent. The vent gases consist primarily of oxygen and nitrogen plus water vapor from the Stretford solution. Minor amounts of ammonia and carbon dioxide and other components absorbed from the Stretford solution may also be present. This emission is not expected to pose a significant environmental problem if adequately dispersed to the atmosphere.

Startup, Shutdown and Upset Gases. During gasifier startup, shutdown, and upsets, gases are produced which do not meet product specifications. If the gas is being burned locally and the customer can safely and economically continue to combust the gas (possibly with auxiliary firing), then this is obviously a good option and really represents a "no control required" situation. If this option is not available, then two possible control strategies may be used. One option is to combust these gases in an incinerator or flare. This option requires installing piping, valves, and instrumentation. A second option is to vent the low-Btu product gas line to the atmosphere through a stack. This option could pose localized odor problems. Therefore, its viability could be limited to those areas where adequate dispersion is attainable.

Water Pollution Control

The uncontrolled effluents from LBG facilities are summarized in Table 3. The pollutants requiring control, factors affecting the effluent characteristics, and estimated effluent flow rates are also summarized in this table. Most of the processes considered for treating these effluents have not been applied to the treatment of low-Btu gasification wastewaters. Therefore, decisions related to the applicability, performance capabilities, and costs of controls were based upon experience gained in related industries including the coking, petroleum refining, and electric utility industries.

Coal Pile Runoff and Ash Sluice Water. These two effluents are very similar to their counterparts in coal-fired power plants. They contain suspended solids and dissolved inorganics but negligible dissolved organics. Treatment techniques used in the utility industry include sedimentation, clarification or filtration for suspended solids removal and acid or base addition for pH adjustment. An additional treatment step available is chemical precipitation for removal of selected trace elements. Use of these techniques for coal pile runoff and ash sluice water from LBG facilities should produce an effluent which would meet the NSPS for coal-fired power plants.

Process Condensate. Process condensate contains suspended solids and dissolved gases, organics, and trace elements. Viable treatment techniques for dissolved organics include activated carbon adsorption and biological oxidation. Sour water strippers can be used to remove dissolved gases. Chemical precipitation treatment can be used to reduce the levels of trace elements, although treatment to remove organics will be the key to disposing of this stream in an environmentally acceptable manner.

TABLE 3. UNCONTROLLED EFFLUENTS FROM LOW-BTU GASIFICATION FACILITIES

UNCONTROLLED EFFLUENTS FROM LOW-BTU GASIFICATION FACILITIES	POLLUTANTS OF POTENTIAL CONCERN	FACTORS AFFECTING EFFLUENT CHARACTERISTICS	ESTIMATED EFFLUENT FLOWRATES
Coal Pile Runoff (Model Plants I, II, and III)	Suspended solids (coal fines), inorganics leached from coal, pH	Coal type and conditions of wastewater contact with coal (e.g., residence time) will determine waste stream composition. Rainfall rates and coal storage practices will determine flow.	Flow rate is intermittent and variable. Annual average: 7.5 to 15 kg/min (2 to 4 gpm). Average from 10 year/24 hour rain: 380 to 760 kg/min (100 to 200 gpm).
Ash Sluice Water (Model Plants I, II, and III which use Wellman-Galusha gasifier)	Suspended solids, inorganics and trace elements leached from ash	Characteristics of the ash and contact time between the ash and sluice water will determine waste stream composition. Quantity of ash removed from gasifier and operator practices will determine flow.	Flow rate is intermittent, existing only when ash is removed. This is normally 2 or 3 times per day, per gasifier. Average flow: 20 to 60 kg/min (5 to 16 gpm).
Process Condensate (Model Plants II and III)	Suspended solids, dissolved organics, inorganics, trace elements, and gases	Composition of low-Btu gas has major influence on composition. Important factors include H_2S, HCN, NH_3, and tar/oil content of gas. Chloride content of coal feed and moisture content of gas determine waste flow.	Based on maintaining water balance in quench loop: bituminous coal - 23 kg/min (6 gpm) lignite - 76 kg/min (20 gpm) anthracite - periodic Flows may be as high as 76 kg/min (20 gpm) for all coals in order to control chloride corrosion problems.

Thus two treatment options appear to be available for treating process condensate: one uses carbon adsorption and steam stripping while the other uses biological oxidation and steam stripping. Chemical precipitation could be used with either option. For both of the options, the organics removal unit is required only if the coal feed produces tars and oils when gasified. Since anthracite does not produce tars and oils, the treatment of condensate from an anthracite gasifier may not require dissolved organics removal. Representative performance criteria for two treatment options for process condensate are summarized in Table 4.

TABLE 4. ESTIMATED PERFORMANCE CAPABILITIES OF PROCESS CONDENSATE TREATMENT TECHNOLOGIES

Component	Untreated Effluent	Treated Effluent[a]	Treated Effluent[b]
TSS	140	<10	<30
Oil and Grease	400	<10	<30
BOD	9000	?	<1000
Phenols	2000	<5	<20
TOC	5600	<700	<700
NH_3	4000	<50	<50
H_2S	220	<10	<10
CN^-	1100	<10	<10
Trace Elements	Yes	some removal[c]	some removal[c]

Unit: mg/l

[a] Treatment using activated carbon adsorption and steam stripping.

[b] Treatment using biological oxidation and steam stripping.

[c] Increased removals of cationic trace elements can be achieved using chemical precipitation.

Solid Waste Management Alternatives

The solid wastes generated by low-Btu gasification facilities are summarized in Table 5. Included in this table are estimated flow rates, important characteristics (such as physical condition, energy content, potential environmental problems), and expected classification (as hazardous or nonhazardous) for each waste. Management techniques for these wastes should be based on the criteria and guidelines developed by the EPA in response to the Resource Conservation and Recovery Act.

Coal Fines. Generally, coal fines are not expected to be a waste produced by low-Btu gasification facilities. This is because presized coal is normally purchased, eliminating the need for on-site crushing and sizing. However, it is possible that final, on-site sizing may be required if fuel size degradation occurs in shipment and handling. If so, a coal fines stream will be produced. The quantity of fines produced is difficult to estimate but

TABLE 5. UNCONTROLLED WASTES FROM LOW-BTU GASIFICATION FACILITIES

Waste	Flow Rate	Characteristics	Expected Classification
Coal Fines (All Model Plants)	This is not a waste stream unless on-site sizing is employed. Flow rates have not been estimated.	Dry solid; heating value same as coal feed.	Non-hazardous
Gasifier Ash (All Model Plants)	800 to 1800 kg/hr	Damp solid with 20 to 30% H_2O; heating value: 1.4 to 8.2 MJ/kg; leachable trace elements.	Non-hazardous
Cyclone Dust (All Model Plants)	6 to 38 kg/hr	Dry solid; heating value: 25 to 28 MJ/kg; leachable trace elements.	Non-hazardous
Stretford Sulfur Cake (Model Plant III)	70 to 620 kg/hr	Wet solid with approximately 50% H_2O; contains thiocyanates, thiosulfates, iron, vanadates, ADA, EDTA.	Hazardous
Tars ands Oils (Model Plants II and III gasifying non-anthracite coals)	750 to 1220 kg/hr	Viscous liquid; specific gravity greater than one; heating value: 30 to 37 MJ/kg; contains organics and trace elements.	Hazardous

should be very small. Since coal fines have the same energy content as coal, a desirable means of handling them is to recover their energy value. Because of the small quantities involved, this may be practical only if an existing combustor is available on-site or nearby. If resource recovery is not practical, then the coal fines should be disposed of as a nonhazardous waste in a sanitary landfill.

Gasifier Ash. Gasifier ash is the unreacted portion of the coal fed to the gasifier - predominantly mineral matter but also some carbonaceous material. After dewatering, it is a damp solid containing 20 to 30 weight percent water. All available data on gasifier ash indicate that it is a nonhazardous waste. As such, the most reasonable option for disposing of gasifier ash is disposal in a sanitary landfill.

Cyclone Dust. Cyclone dust resembles devolatilized coal. It has a carbon content as high as 90 percent and a heating value of 25 MJ/kg (11,000 Btu/lb) or higher. It is removed from the cyclones as a dry, powdery solid. All available data indicate that cyclone dust is a nonhazardous waste and could be disposed of in a sanitary landfill. Because of its high energy content though, consideration should be given to recovering its fuel value.

Stretford Sulfur Cake. Elemental sulfur is produced by a Stretford unit and recovered as a filter cake containing approximately 50 percent water. No test data are available for this waste. However, it will contain Stretford solution chemicals (vanadates, anthraquinone disulfonic acid salts, EDTA, and iron) and nonregenerable sulfur components such as thiocyanates and thiosulfates. Because of the presence of these contaminants, Stretford sulfur cake is suspected to be a hazardous waste. If so, the management technique for this waste would have to comply with the Subtitle C criteria and guidelines for hazardous waste disposal. Alternatively, the contaminated sulfur can be processed to recover a saleable by-product. This option produces an effluent containing the contaminants originally present in the sulfur cake. Reductive incineration and high temperature hydrolysis are two techniques recently developed for treating Stretford solution effluent, but these approaches are not proven commercially.

Tars and Oils. By-product tars and oils contain a number of toxic organics. However, due to the high specific gravity and viscosity of this material, it is expected to have a low vapor pressure which will minimize the release of volatile organics during storage. Operators and handlers should take precautionary steps to minimize contact with this material. Special note should be taken of the NIOSH proposed criteria for coal gasification plants. Because of its significant fuel value, the logical management technique for by-product tars and oils is resource recovery. This would involve using the material to fire a boiler or furnace.

SUMMARY OF POLLUTION CONTROL COSTS AND ENERGY REQUIREMENTS

In order to compare controls for cost effectiveness and to estimate the impact of pollution control costs on overall plant costs, approximate capital and operating costs for individual control processes/equipment were developed. These costs are based primarily on factored estimates of costs contained in non-proprietary published literature, normalized to a first quarter 1980 basis. In some cases actual vendor quotes have been used but generally, it was beyond the scope and purpose of the background studies to develop the detailed engineering designs necessary for cost estimation at the "firm" (approaching ± 10 percent) level. Although the accuracy of the cost estimates varies, most are believed to be within 50 percent.

For purposes of presentation in this paper, costs for various pollution control options are given as a percent of the "uncontrolled" plant capital and total annualized costs. This format was selected since it more clearly indicates the magnitude of pollution control costs on overall plant costs than would actual dollar estimates. This approach has the additional benefit of being less sensitive to assumed economic factors such as inflation, interest rates (cost of capital), etc.

Total annualized costs were calculated as the sum of annual operating cost and annualized capital costs. For purposes of annualizing the capital investment, a fixed rate charge factor of 0.175 was calculated. This represents the fraction of the total capital investment that must be assessed as annualized capital charge.

Table 6 summarizes the capital and annualized cost impacts of pollution control for the three model plants examined. The ranges shown reflect differences in control costs as a result of gasifying the four coals studied. They are not intended to reflect the accuracy of the cost impacts. All cost numbers are expressed in terms of a percent of the uncontrolled base plant costs.

As shown in this table, the cost impacts for emission controls are minimal. Capital costs or annualized costs do not exceed 2 percent of the base plant cost for any emission and, most of the control costs are below 1 percent. On a total plant basis, the emission controls are estimated to add approximately 1 to 3 percent to the base plant capital requirements and increase annualized costs by 2 to 5 percent. Energy requirements for air pollution control are negligible.

The cost impacts for controlling a specific liquid effluent are greatest for the hot gas systems and least for the desulfurized gas systems. This reflects an increase in the base plant costs and not a decrease in the control costs. Total plant water treatment costs tend to increase or remain approximately constant as the degree of gas purification increases. This reflects the fact that increases in the base plant costs (the denominator used to calculate the percentage cost impacts shown) are offset by increased treatment costs (the

TABLE 6. SUMMARY OF ESTSIMATED POLLUTION CONTROL COST IMPACTS[a]

	Control Costs as a Percent of Base Plant Costs					
	Hot Gas		Cooled Gas		Desulfurized Gas	
	Capital	Annualized	Capital	Annualized	Capital	Annualized
GASEOUS EMISSIONS						
Coal Feeder Gases	0.8-1.0	0.9- 1.7	0.6- 0.9	0.8- 1.6	0.3-0.6	0.6- 1.3
Pokehole Gases	1.0-1.2	1.1- 2.0	0.7- 1.0	0.9- 1.9	0.4-0.8	0.7- 1.6
Stretford Oxidizer	-	-	-	-	none	none
Transient Gases	0.8-1.0	1.1- 1.4	0.7	1.0- 1.3	0.4-0.5	0.7- 1.1
TOTAL	2.8-3.0	3.1- 5.1	2.0- 2.6	2.7- 4.8	1.1-1.9	2.0- 4.0
LIQUID EFFLUENTS						
Coal Pile Runoff Ash Sluice Water	2.8-10.3	1.2- 2.6	2.4- 7.3	1.1- 2.3	1.7-4.1	0.9- 1.7
Process Condensate	-	-	1.5- 7.9	1.4- 6.8	1.1-4.4	1.2- 5.1
TOTAL	2.8-10.3	1.2- 2.6	3.9-15.2	2.5- 9.1	2.8-8.5	2.1- 6.8
SOLID WASTES						
Gasifier Ash	b	4.6- 7.3	b	4.1- 6.7	b	2.8- 5.4
Cyclone Dust	b	<0.1- 0.2	b	<0.1- 0.2	b	<0.1- 0.1
Sulfur Cake	-	-	-	-	b	0.6- 6.2
Tars and Oils	-	-	c	c	c	c
TOTAL	b	4.8- 7.5	b	4.3- 6.8	b	4.5- 9.1
TOTAL POLLUTION CONTROL	5.8-13.1[b]	9.5-13.9	6.5-17.2[b]	11.9-18.1	4.6-9.6[b]	9.5-17.2

a - Ranges shown reflect differences in control costs for various coal feeds. Totals shown are ranges calculated from totals for each coal feed, which may be different than algebraic sum of component ranges shown.

b - Data not available for capital costs for solid waste disposal.

c - No costs are included for controlling tars and oils; recovery of fuel value is expected.

(-) - Discharge does not exist for this model plant.

numerator used to calculate the cost impacts) resulting from the need to treat additional effluents. On a total plant basis, water pollution control costs are estimated to increase the base plant capital costs by 3 to 15 percent and annualized costs by 1 to 9 percent. Energy requirements for water pollution control amount to 0.6 to 2.1 percent of the energy content of the low-Btu product gas. This is almost entirely attributable to the sour water stripper steam requirements for treating process condensate.

Capital cost estimates were not available for the solid waste disposal practices. The waste disposal annualized costs are dominated by the costs of handling gasifier ash, with the only other significant costs being those associated with sulfur cake disposal. (For the high sulfur bituminous coal case, sulfur disposal costs are dominant). Cost factors used for disposal of wastes were \$21 and \$71 per metric ton for nonhazardous and hazardous wastes, respectively. Although \$71 per tonne is a relatively high estimate for hazardous waste dispoal, it may not truly reflect the costs associated with disposing of very small quantities of hazardous wastes. For small quantities, the relative impacts of capital costs and administrative costs (in terms of dollars per tonne disposed) can be very large.

Energy requirements for disposing of solid wastes are minimal and are estimated at 0.2% or less of the low-Btu gas energy content. The energy requirements are mainly fuel for haul trucks and earthmoving equipment.

The total plant pollution control cost impacts are estimated to range from approximately 6 to 17 percent of the base plant capital investment and from 9.5 to slightly over 18 percent of the base plant's annualized costs.

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DEVELOPMENT OF A
POLLUTION CONTROL GUIDANCE DOCUMENT
FOR INDIRECT COAL LIQUEFACTION

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ABSTRACT

Synfuels present both an opportunity and a problem for EPA in terms of developing a new environmentally acceptable industry. The opportunity is for EPA to encourage environmental controls to be incorporated/developed as an integral part of the first plant designs rather than as "add on" technology in an existing industry. The problem is that an adequate data base for promulgation of defensible regulations for synfuels plants does not now exist and will likely not exist until after the first plants have been constructed and operated for some period of time. EPA has responded to this situation with the "Pollution Control Guidance Document (PCGD)" concept, in which the best thinking of the various EPA R&D program and regional offices is to be provided to permitters and to industry in the form of "guidance" for an interim period rather than as regulations.

The Indirect Liquefaction (IL) PCGD is one of the first such documents which EPA is preparing with the technical support of various contractors. TRW, Radian, Versar and RTI are involved in the preparation of the data base for the first technical draft of the ILPCGD.

This paper summarizes the technology basis for control levels identified.

DEVELOPMENT OF A POLLUTION CONTROL GUIDANCE DOCUMENT FOR INDIRECT COAL LIQUEFACTION

The production of transportation fuels from domestic coal to displace fuels derived from imported petroleum has high priority in the overall U.S. energy policy. Since indirect liquefaction (IL) is the only commercially demonstrated means of producing transportation fuels from coal, this technology is likely to be among the first to be employed for synthetic fuels production in the United States.

The Environmental Protection Agency (EPA) is responsible for ensuring that the designs of first generation synthetic fuel technologies provide for adequate protection of the environment. To serve this need and to avoid costly delays in the commercialization of a process due to uncertainties concerning environmental control requirements, EPA developed the Pollution Control Guidance Document (PCGD) approach. This paper summarizes the data base that has been developed for the preparation of the PCGD for Lurgi-based IL technology. EPA's technical support contractors in this effort are TRW, Radian, Versar, and RTI.

The approach for the ILPCGDs was to develop a series of model plants based on Lurgi, Texaco, and Koppers-Totzek (K-T) gasification using methanol, Fischer-Tropsch (F-T), and Mobil M-gasoline synthesis. These technologies are considered commercial or near-commercial. Major and minor constituent material balances were established for integrated model plants using three U.S. coals (Montana Rosebud subbituminous, Illinois No. 6 bituminous, and North Dakota lignite) in order to provide estimates of the volumes and loadings of various waste streams which would be generated. Waste stream constituents covered by the PCGD include both conventional/criteria/consent decree pollutants and currently unregulated substances (e.g., POM).

The PCGD data base includes an identification and evaluation of various pollution control options, based on the expected capabilities of available technologies, for all major gaseous, aqueous, and solid waste streams generated in an integrated facility. This paper presents several of the control options developed in the data base. The control options are based on considerations of the volume and toxicity of the specific waste stream, costs, safety, reliability, degree to which controls have been demonstrated, intra- and intermedia tradeoffs, and site specific factors.

The major sources of data used in the Lurgi data base for defining the types and characteristics of uncontrolled indirect liquefaction plant waste streams are (1) data obtained as part of an EPA sponsored environmental test program of a Lurgi gasification facility at Kosovo, Yugoslavia; (2) data obtained as part of an Energy Research and Development Administration (ERDA, now DOE) sponsored program involving the gasification of American coals in a Lurgi gasifier at Westfield, Scotland; (3) data obtained as part of an American Natural Gas, Inc. sponsored program involving gasification of North Dakota lignite at the SASOL plant in South Africa; (4) data provided to EPA by South African Coal and Gas Corp. Ltd. (SASOL); and (5) data contained in various permit filings and environmental impact statements for proposed Lurgi-based SNG and indirect liquefaction facilities in the U.S.

Data sources employed for development of model plant/process configurations were primarily engineering studies of the technology sponsored by DOE, EPA, and EPRI. Data sources which served as the basis for the analysis of pollution control applicability and costs include the above engineering studies, studies conducted by TVA, various permit filings, technical information obtained from pollution control equipment vendors and process developers, and published literature. Much of the information on controls is derived from applications in related industries such as petroleum refining, natural gas processing, by-product coke production, electric utilities, and coal preparation.

The configurations of the model plants were based on designs of Lurgi plants which are either proposed or currently in operation. Auxiliary processes considered were those which would render a facility essentially self-sufficient in energy (one which would need only run-of-mine coal, raw water, and various chemicals and catalysts as inputs). A plant size corresponding to 1×10^{11} Btu/day (2.5×10^{10} kcal/day) of total product was selected as representative of the first plant(s) which may be built. This corresponds to about 7000 bbls/day (1200 Nm^3/day) gasoline plus 50×10^6 SCF (1.3×10^6 Nm^3) of substitute natural gas per day (co-produced in the case of Lurgi gasification). This is approximately the size of the first phase facility planned by American Natural Resources for their North Dakota SNG project.

Figures 1 and 2 are simplified flow diagrams of the main process train and auxiliary operations associated with integrated Lurgi IL facilities. System operations include coal preparation, coal gasification, gas purification and upgrading, crude product synthesis and separation, and product upgrading. Nonpollution control auxiliary processes include process cooling, product storage, raw water treatment, steam and power generation, and oxygen production. The major waste streams identified for facilities depicted in the figures are listed in Table 1 along with the primary constituents/parameters of concern for each waste. The remainder of this paper will focus on control options for these major streams in Lurgi-based facilities. Note that no fundamentally new problems are believed to apply to K-T or Texaco gasification which do not also apply to Lurgi gasification, although differences do exist in the relative quantities of wastes/waste constituents which are generated. Indeed, K-T and Texaco gasification may be somewhat less complicated than Lurgi since the former gasifiers generate fewer organics (other than methane and formic acid) which would eventually become components of waste streams. The organics in Lurgi wastes present some of the more difficult pollution control problems.

Gaseous Waste Streams

Figure 3 summarizes the primary control options for Lurgi acid gases. Indicated in the figure are both selective and nonselective Rectisol* acid gas removal (AGR); that is, separate removal of CO_2 and H_2S from product gas generating an H_2S-rich stream and a CO_2-rich stream or combined removal generating only one dilute H_2S stream. The primary goal of selective AGR is to produce a more concentrated sulfur-bearing stream for sulfur recovery allowing either the use of Claus technology or the reduction in a Stretford plant size (and thus reduced cost). Since selective AGR is significantly more expensive than nonselective AGR, it is economically justified only if cost savings are realized in sulfur recovery/pollution control. If, for environmental reasons, the CO_2-rich stream from selective AGR cannot be directly discharged to the atmosphere (with perhaps incineration), then treatment

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*Rectisol is a Lurgi-licensed acid gas removal (AGR) process and would be used with all Lurgi gasifiers in the U.S.

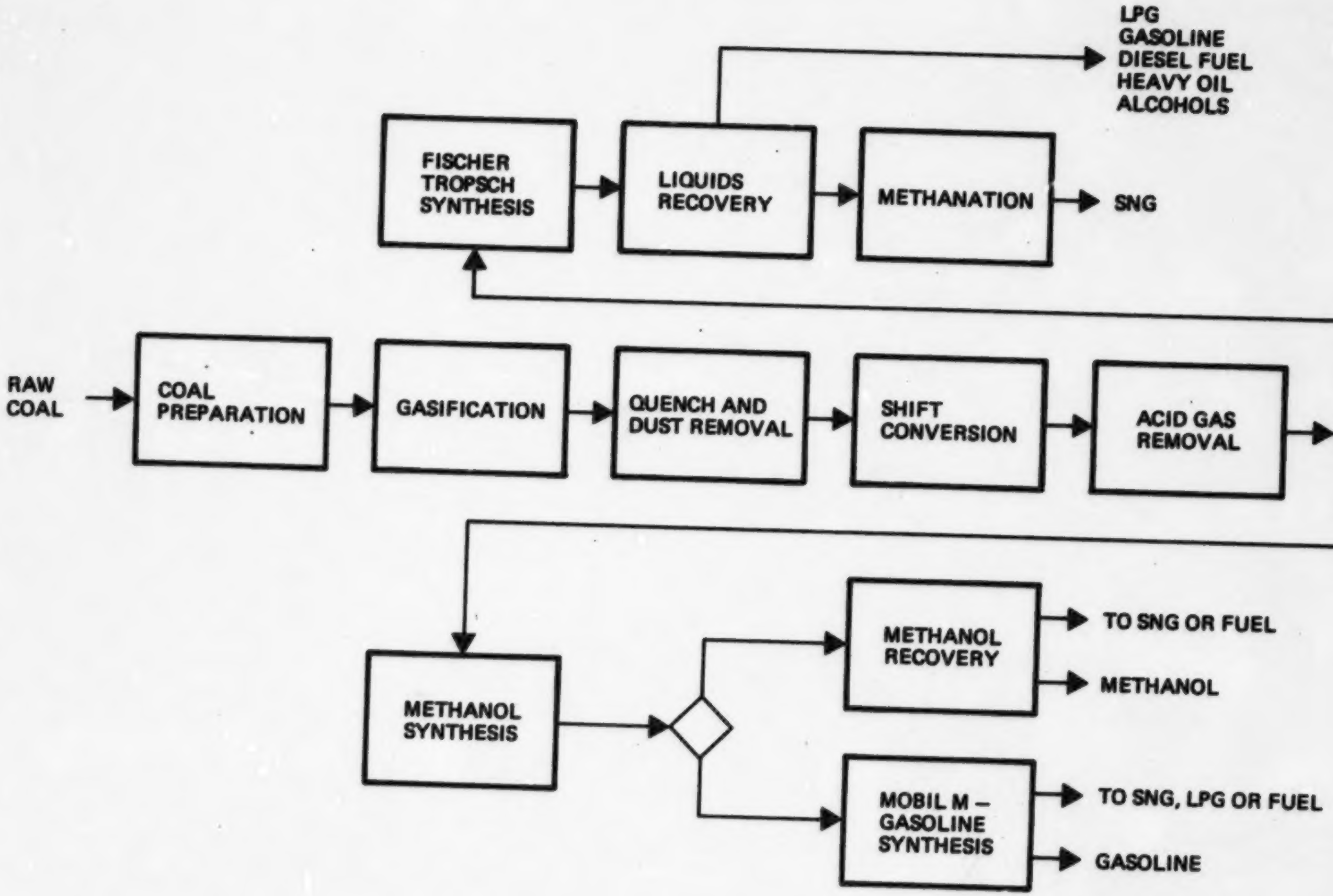
RAW COAL
COAL PREPARATION
GASIFICATION
QUENCH AND DUST REMOVAL
SHIFT CONVERSION
ACID GAS REMOVAL
FISCHER TROPSCH SYNTHESIS
LIQUIDS RECOVERY
METHANATION
LPG
GASOLINE
DIESEL FUEL
HEAVY OIL
ALCOHOLS
SNG
METHANOL SYNTHESIS
METHANOL RECOVERY
MOBIL M – GASOLINE SYNTHESIS
TO SNG OR FUEL
METHANOL
TO SNG, LPG OR FUEL
GASOLINE

Figure 1. Simplified Flow Diagram of Indirect Coal Liquefaction Facilities

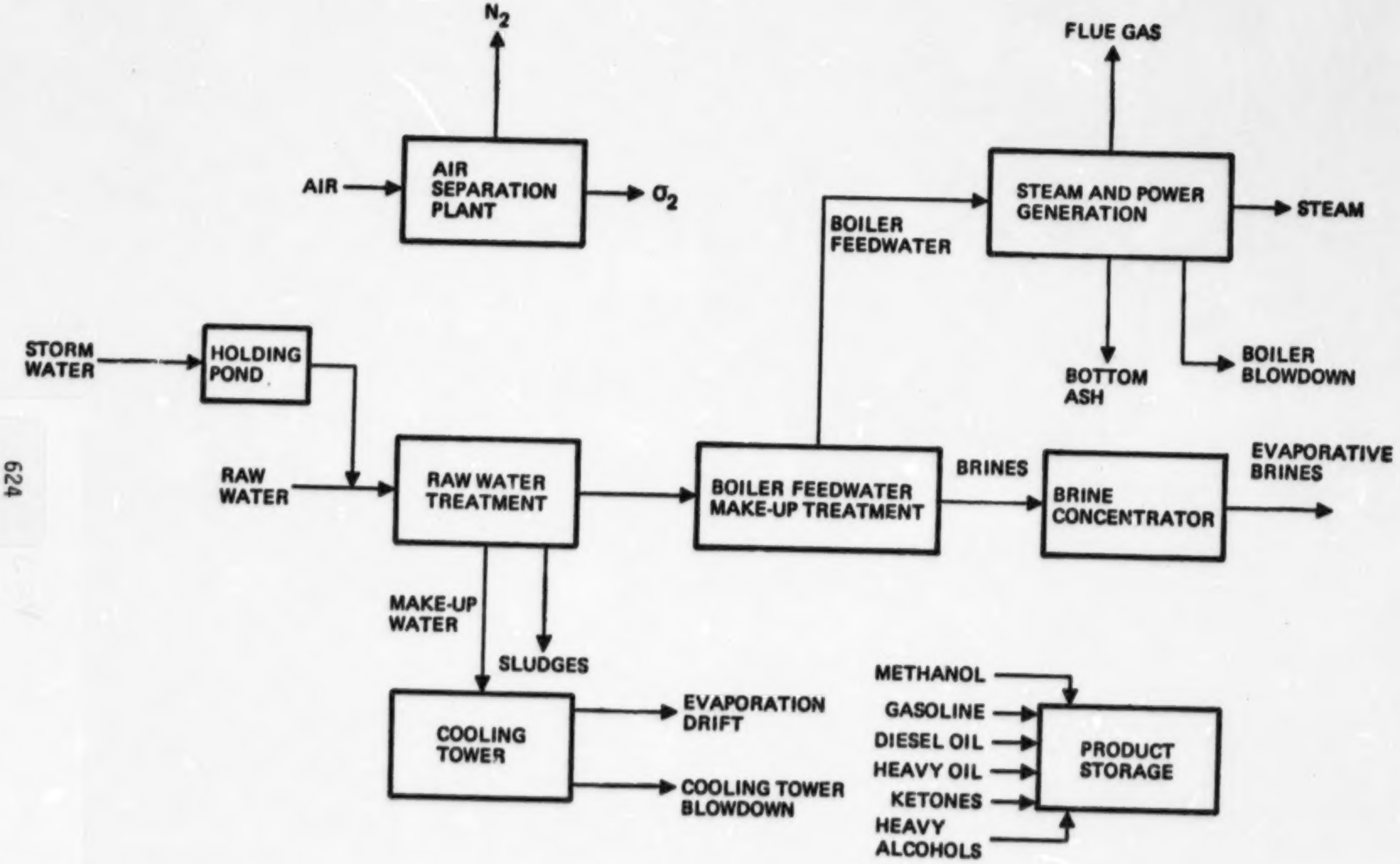
N$_2$
AIR
AIR SEPARATION PLANT
O$_2$
FLUE GAS
STEAM AND POWER GENERATION
STEAM
BOILER FEEDWATER
BOTTOM ASH
BOILER BLOWDOWN
STORM WATER
HOLDING POND
RAW WATER
RAW WATER TREATMENT
BOILER FEEDWATER MAKE-UP TREATMENT
BRINES
BRINE CONCENTRATOR
EVAPORATIVE BRINES
MAKE-UP WATER
SLUDGES
COOLING TOWER
EVAPORATION DRIFT
COOLING TOWER BLOWDOWN
METHANOL
GASOLINE
DIESEL OIL
HEAVY OIL
KETONES
HEAVY ALCOHOLS
PRODUCT STORAGE

Figure 2. Auxiliary Operations Associated with an Indirect Coal Liquefaction Facility

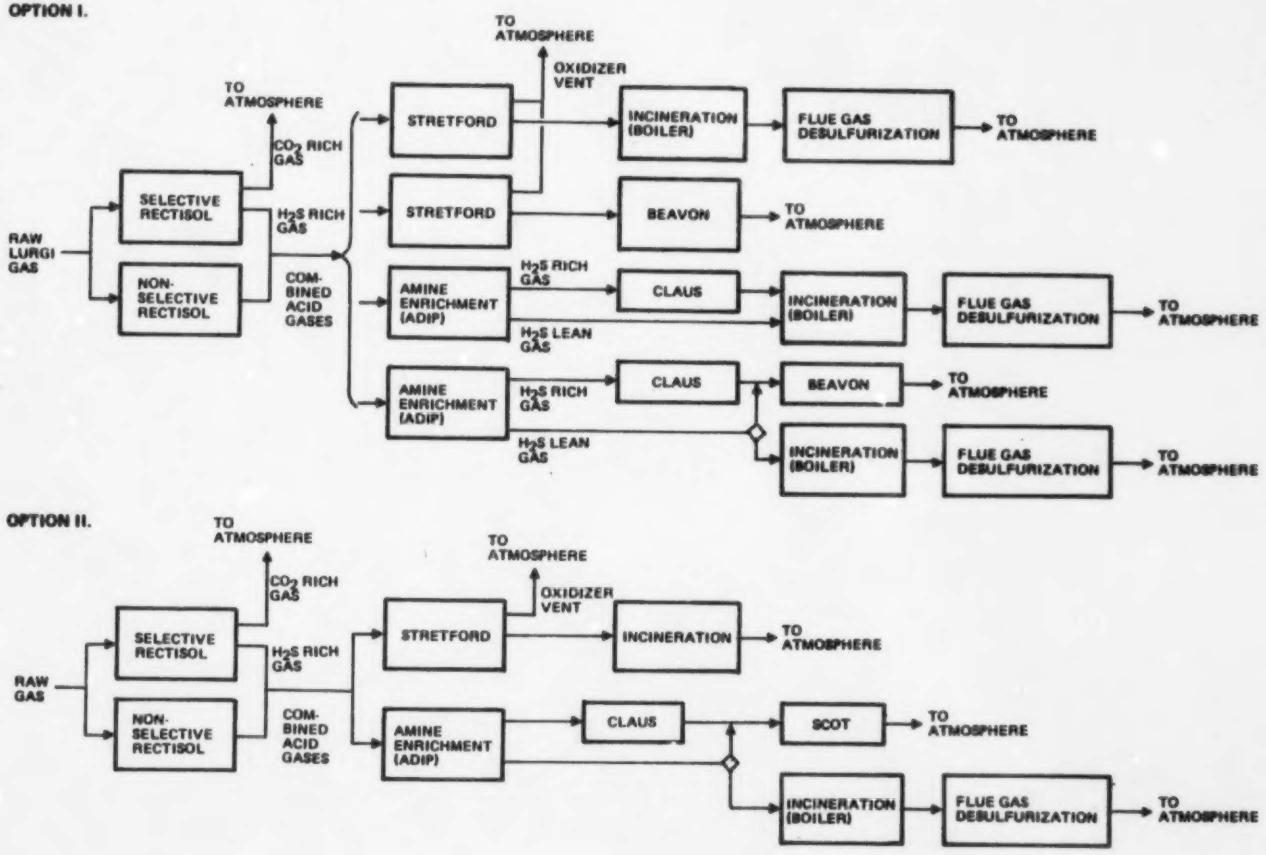
OPTION I.
RAW LURGI GAS
SELECTIVE RECTISOL
NON-SELECTIVE RECTISOL
TO ATMOSPHERE
CO_2 RICH GAS
H_2S RICH GAS
COM-BINED ACID GASES
STRETFORD
STRETFORD
AMINE ENRICHMENT (ADIP)
AMINE ENRICHMENT (ADIP)
TO ATMOSPHERE
OXIDIZER VENT
H_2S RICH GAS
H_2S LEAN GAS
H_2S RICH GAS
H_2S LEAN GAS
INCINERATION (BOILER)
BEAVON
CLAUS
CLAUS
FLUE GAS DESULFURIZATION
TO ATMOSPHERE
TO ATMOSPHERE
INCINERATION (BOILER)
BEAVON
INCINERATION (BOILER)
FLUE GAS DESULFURIZATION
TO ATMOSPHERE
TO ATMOSPHERE
FLUE GAS DESULFURIZATION
TO ATMOSPHERE
OPTION II.
RAW GAS
SELECTIVE RECTISOL
NON-SELECTIVE RECTISOL
TO ATMOSPHERE
CO_2 RICH GAS
H_2S RICH GAS
COM-BINED ACID GASES
STRETFORD
AMINE ENRICHMENT (ADIP)
TO ATMOSPHERE
OXIDIZER VENT
INCINERATION
TO ATMOSPHERE
CLAUS
SCOT
TO ATMOSPHERE
INCINERATION (BOILER)
FLUE GAS DESULFURIZATION
TO ATMOSPHERE

Figure 3. Options for Control of Lurgi/Rectisol Acid Gases

TABLE 1. MAJOR WASTE STREAMS IN AN INTEGRATED INDIRECT LIQUEFACTION FACILITY

WASTE STREAMS	PRIMARY CONSTITUENTS/PARAMETERS OF CONCERN
GASEOUS STREAMS	GASEOUS STREAMS
• ACID GASES (INCLUDING STRIPPING AND DEPRESSURIZATION GASES)	• REDUCED SULFUR AND NITROGEN COMPOUNDS, HYDROCARBONS
• BOILER FLUE GASES	• SULFUR DIOXIDE, PARTICULATES, NITROGEN OXIDES
• TRANSIENT WASTE GASES • FEED LOCKHOPPER VENT GASES	• REDUCED SULFUR AND NITROGEN COMPOUNDS, HYDROCARBONS, CARBON MONOXIDE, PARTICULATES, POLYCYCLIC ORGANIC MATERIAL
• CATALYST REGENERATION/DECOMMISSIONING OFFGASES	• SULFUR DIOXIDE, PARTICULATES, CARBON MONOXIDE, TRACE ELEMENTS
AQUEOUS STREAMS	AQUEOUS STREAMS
• RAW GAS QUENCH AND ACID GAS REMOVAL CONDENSATES	• ORGANIC COMPOUNDS, SUSPENDED SOLIDS, CYANIDES AND THIOCYANATES, AMMONIA, TRACE ELEMENTS
• ASH QUENCH BLOWDOWN	• DISSOLVED AND SUSPENDED SOLIDS, TRACE ELEMENTS
• SYNTHESIS WASTEWATERS	• ORGANIC COMPOUNDS
• WASTEWATER TREATMENT BRINES	• DISSOLVED AND SUSPENDED SOLIDS, TRACE ELEMENTS
SOLID WASTES/SLUDGES	SOLID WASTES/SLUDGES
• GASIFIER ASH	• SOLUBLE SALTS, TRACE ELEMENTS
• BOILER ASH	• SOLUBLE SALTS, TRACE ELEMENTS
• FGD SLUDGES AND BRINES	• SOLUBLE SALTS, TRACE ELEMENTS
• WASTEWATER TREATMENT BRINES	• SOLUBLE SALTS AND ORGANICS, TRACE ELEMENTS
• BIOSLUDGES	• SOLUBLE ORGANICS, TRACE ELEMENTS
• SPENT CATALYSTS	• TRACE ELEMENTS

costs for this stream would likely make the selective AGR option unattractive and designers may revert to nonselective modes.

Option I in Figure 3 consists of Stretford or Claus sulfur recovery followed by tail gas treatment (TGT) for residual sulfur removal and hydrocarbon control. In the Claus cases, enrichment of the H_2S feed stream may be required or desired and an amine (ADIP) system is indicated in the figure. The ADIP offgas and the Claus offgas both receive TGT prior to atmospheric discharge; the CO_2 rich gas from selective AGR is directly discharged to the atmosphere. TGT technologies include incineration/FGD (e.g., Wellman-Lord) and catalytic reduction H_2S recycle (e.g., Beavon).

The Option II alternatives consist of either Stretford sulfur recovery followed by incineration for hydrocarbon control or Claus sulfur recovery followed by SCOT TGT. Neither Claus without sulfur TGT nor direct incineration followed by flue gas desulfurization is considered adequate under Option II since neither of these controls achieves the same levels of total sulfur emissions compared to Stretford or Claus/SCOT. Note that the alternatives in Figure 3 represent the range of controls envisioned by all conceptual and proposed Lurgi gasification projects in the U.S. which have been identified to date.

Table 2 summarizes the estimated costs and energy requirements for control of acid gas in integrated facilities. The cost data represent the least expensive system in each option but assume no credit for energy recovery from incineration of Lurgi gases. Total annualized costs range from 3.8 to 5.7% of base plant costs for sulfur recovery with TGT compared to 2.3 to 4.0 for sulfur removal only (Stretford). Energy requirements of control of acid gases vary from essentially zero to 1.9% of plant input energy, depending primarily on the extent of heat recovery practiced during incineration. Recovered energy could exceed that required to operate the sulfur control systems.

Options for the control of boiler flue gas emissions correspond to the levels defined by electric utility NSPS (Option I) and large industrial boiler NSPS (Option II). Table 3 summarizes the SO_2, particulates, and NO_x options. For gaseous and liquid fuels derived from coal (e.g., tars, oils, phenols, naphtha, low Btu gas), the same limits apply as to the petroleum or natural gas fuels.

TABLE 2. RELATIVE COSTS AND ENERGY REQUIREMENTS FOR CONTROL OF ACID GASES (AS PERCENT OF BASE PLANT COST OR ENERGY INPUT)

	Low Sulfur Coal			High Sulfur Coal		
	Capital	Total Annual	Energy	Capital	Total Annual	Energy
Option I (Sulfur removal plus tail gas treatment)	3.2	3.8	0 -0.84	5.3	5.7	0 - 1.9
Option II (Sulfur removal, minimum or no tail gas treatment)	1.6	2.3	0 - 0.8	3.0	4.0	0 - 1.8

TABLE 3. CONTROL OPTIONS FOR COAL BOILER SO_2, PARTICULATE, AND NO_x EMISSIONS

	Option I $g/10^6$ cal ($lb/10^6$ Btu)	Option II $g/10^6$ cal ($lb/10^6$ Btu)
SO_2	2.16 (1.2) and 90% control unless emissions less than 1.09 (0.6) in which case 70% required	2.16 (1.2)
Particulates	0.054 (0.03)	0.18 (0.10)
NO_x Lignite & bituminous coals	1.1 (0.6)	
Subbituminous coals	0.88 (0.5)	1.26 (0.7)
Lurgi byproducts	1.1 (0.6)	

Costs associated with a representative FGD system (Wellman-Lord) applied to a coal- and Lurgi-byproduct-fired boiler are estimated in Table 4. Annualized costs of the FGD systems amount to 2.4 - 3.9% of base plant costs, depending on the boiler size, coal sulfur content, and degree of SO_2 removal attained. Energy requirements for the example FGD units range from 2.9 to 5.8% of the boiler heat input, or 0.4 to 0.6% of total plant input energy. Note that incremental costs for FGD sulfur removal are about $11-15/lb ($24-33/kg) while incremental costs for sulfur recovery FGT sulfur removal are about $20-30/lb ($44-66/kg). Thus, it may be less expensive to design for lower emissions at the boiler rather than lower emissions from sulfur recovery operations if minimum overall sulfur emissions control at least cost is a defined goal and is environmentally acceptable.

Table 5 summarizes the control options for smaller volume waste streams in Lurgi indirect liquefaction facilities. Generally, the controls for these streams consist of incineration with or without additional SO_2 and/or particulate control.

Aqueous Waste Streams

Figure 4 presents the major options evaluated for control of gasification and synthesis wastewaters. Lurgi wastewaters (gas liquors) are treated for tar/oil separation, phenol removal (Phenosolvan), and ammonia removal as basic steps in all cases. Further treatment would consist of biological or chemical oxidation for bulk organics removal and chemical precipitation and carbon absorption for trace elements and refractory organics removal when discharge to surface waters is the wastewater disposal method (Option I). When "zero discharge" to surface waters is to be practiced, treatment would consist of volume reduction via use of cooling towers, evaporators, and/or incinerators. Biological oxidation may precede the cooling tower concentration step. Ultimate disposal of residual brines may be via underground injection (Option II), surface impoundment (Option III), and ash quenching (Option IV).

The "zero discharge" options involve various tradeoffs with air emissions (cooling tower evaporation/drift) or solid waste disposal (leaching of organics or trace elements in surface impoundments or landfills). In the case of codisposal of brines with ash, the combined waste may be rendered hazardous due to the residual organics or trace elements contained in the brine.

TABLE 4. SO_2 EMISSIONS, COSTS, AND ENERGY REQUIREMENTS ASSOCIATED WITH BOILER/WELLMAN-LORD FGD SYSTEMS

	Sulfur Removal (%)	SO_2 Emissions (kg/10^6 kcal)	Costs			Energy*** Requirements (%)
			Capital	Annual		
			(%)**	(%)**	($/kg S Removed)	
Low Sulfur (Rosebud)	70	0.88	2.6	2.7	9.7	2.9
	80	0.58	4.0	3.9	12.0	3.2
High Sulfur (Illinois No. 6)	80	0.98	2.5	2.4	9.2	5.2
	90	0.51	3.2	3.6	12.0	5.8

*Coal to boiler

**Percentage of uncontrolled base plant costs.

***As percentage of coal fed to boiler

TABLE 5. CONTROL OPTIONS FOR SMALL VOLUME LURGI WASTE GASES

	Feed Lock Vent Gases	Transient Waste Gases	Catalyst Decommissioning Offgases
Option I	Recompression/recycle or use as fuel for high pressure gases, incineration of low pressure residuals	Incineration with SO_2 and particulate control	Incineration with SO_2 and particulate control
Option II	Discharge of residuals via low energy scrubber	Incineration, short term discharge of high oxygen content waste gases	Incineration

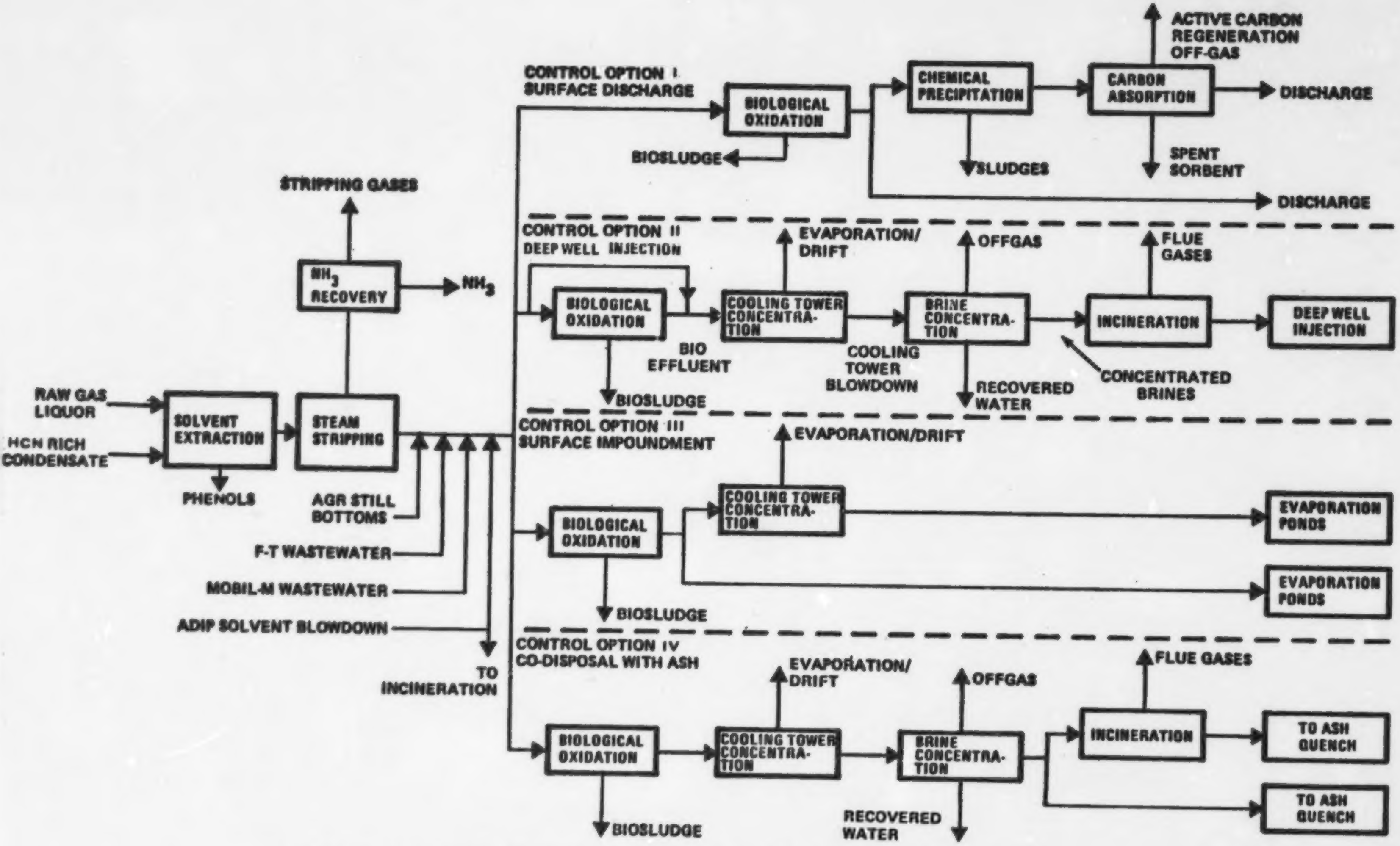
RAW GAS LIQUOR
HCN RICH CONDENSATE
SOLVENT EXTRACTION
PHENOLS
STEAM STRIPPING
NH3 RECOVERY
STRIPPING GASES
NH3
AGR STILL BOTTOMS
F-T WASTEWATER
MOBIL-M WASTEWATER
ADIP SOLVENT BLOWDOWN
TO INCINERATION
CONTROL OPTION I SURFACE DISCHARGE
BIOLOGICAL OXIDATION
BIOSLUDGE
CHEMICAL PRECIPITATION
SLUDGES
CARBON ABSORPTION
ACTIVE CARBON REGENERATION OFF-GAS
SPENT SORBENT
DISCHARGE
DISCHARGE
CONTROL OPTION II DEEP WELL INJECTION
BIOLOGICAL OXIDATION
BIO EFFLUENT
BIOSLUDGE
COOLING TOWER CONCENTRATION
EVAPORATION/ DRIFT
COOLING TOWER BLOWDOWN
BRINE CONCENTRATION
OFFGAS
RECOVERED WATER
CONCENTRATED BRINES
INCINERATION
FLUE GASES
DEEP WELL INJECTION
CONTROL OPTION III SURFACE IMPOUNDMENT
BIOLOGICAL OXIDATION
BIOSLUDGE
COOLING TOWER CONCENTRATION
EVAPORATION/DRIFT
EVAPORATION PONDS
EVAPORATION PONDS
CONTROL OPTION IV CO-DISPOSAL WITH ASH
BIOLOGICAL OXIDATION
BIOSLUDGE
COOLING TOWER CONCENTRATION
EVAPORATION/ DRIFT
BRINE CONCENTRATION
OFFGAS
RECOVERED WATER
INCINERATION
FLUE GASES
TO ASH QUENCH
TO ASH QUENCH

Figure 4. Control Options for Lurgi-based Indirect Liquefaction Plant Wastewaters

Table 6 summarizes the estimated costs and energy requirements for the water pollution control technologies depicted in Figure 4. Although treatment costs are highly coal-, gasifier-, and synthesis-case specific, these estimates indicate the relative contribution of various unit processes to overall costs. The basic treatment steps, phenol removal, ammonia removal, and biological oxidation, constitute 40 to 80% of total treatment costs (or about 3.1% of the base plant annualized costs). Carbon absorption/chemical precipitation is seen as a less expensive route than forced evaporation or surface impoundment for further treatment. The data also indicate that the basic treatment processes also contribute a large fraction of the total energy requirement for water pollution control, with further treatment contributing heavily only with incineration. The use of the cooling tower as a "preconcentration" step has been assumed in the estimates in Table 6; hence treatment of wastewaters by forced evaporation, incineration, or surface impoundment without prior volume reduction could dramatically increase the costs of water pollution control.

Solid/Hazardous Wastes

Options for the disposal of solid wastes generated by the subject facilities are determined both by the characteristics of the waste and by the local environment providing candidate disposal sites. The general operation performance standards for various hazardous waste disposal methods are currently being drafted by EPA's Office of Solid Waste. These standards, based on "best engineering judgment," are expected to largely define the practices for and site-specific factors to be considered in the treatment/disposal of hazardous (and in many cases nonhazardous) wastes. Thus, for purposes of PCGD development, the focus has been on providing a data base for the classification of indirect liquefaction wastes based on their characteristics.

Perhaps the most important waste from the standpoint of volume in the subject facilities is gasifier ash. Several papers presented at this symposium have provided data on the leaching characteristics of ash from a variety of gasifiers and coal types. Generally, these data suggest that gasifier ash is not expected to be hazardous based upon the RCRA Extraction Procedure* test. Thus, this material will likely be handled in a manner

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*Refers to the Extraction Procedure defined in 40 CFR 261.

TABLE 6. TYPICAL COSTS AND ENERGY REQUIREMENTS OF WATER POLLUTION CONTROL TECHNOLOGIES

	Cost*		Energy** Requirements
	Capital	Annual	
Phenosolvan	1.2	1.4	1.3
NH_3 Stripping	0.9	0.6	2.9
Biological oxidation	1.4	1.1	0.1
Chemical precipitation	0.5	0.4	0.04
Carbon adsorption	0.3	0.2	0.01
Forced evaporation	1.3	1.1	0.2
Incineration	0.3	0.3	0.9
Deep well injection	0.2	-	-
Evaporation ponds	7.1	4.3	-

*As percentage of uncontrolled base plant costs
**As percentage of total base plant coal energy input

similar to boiler bottom ash and FGD sludges in the electric utility industry. Limited data indicate that when such wastes are to be disposed of in surface mines that placement should be in "V-notch" areas of the spoil pile rather than in the pit bottom to minimize leaching.

Two important wastes are potentially generated by wastewater treatment (WWT) brines from evaporators or incinerator scrubbers and sludges from biological treatment. In the case of the former, codisposal with gasifier or boiler ash is commonly proposed (codisposal with some type of solid material would be required in any case since RCRA guidelines prohibit the disposal of free flowing liquids in landfills). Codisposal of WWT brines with ash is believed to render the ash hazardous if the organics are not previously destroyed by incineration or wet oxidation. However, if the organics in the brine are destroyed prior to codisposal, available data indicate that the ash/brine mixture would be classified as nonhazardous according to the RCRA Extraction Procedure test. Thus, a tradeoff may exist between WWT costs for organics destruction and solid (hazardous) waste disposal costs for hazardous vs. non-hazardous disposal. WWT brines may also be disposed of in surface impoundments or by underground injection consistent with RCRA requirements. In the later case, organics in the waste may have to be destroyed prior to injection to prevent plugging of the accepting formation.

Biosludges from WWT would likely be considered a hazardous waste under RCRA. Options for disposal include landfarming, incineration with air pollution control, landfill or mine disposal, and surface impoundment. Dewatered sludges may be beneficially utilized by landfarming in conjunction with revegetation of surface mine spoil overburden.

Several types of spent catalyst wastes are generated in indirect liquefaction facilities, including those from shift synthesis (methanol, F-T, Mobil), methanation, and air pollution control (Claus, Beavon). Wastes such as spent shift catalyst are expected to be hazardous due to their inherent metal content as well as other toxic elements derived from coal. Wastes such as Mobil-M (a zeolite material) and Claus (Bauxite) spent catalysts are not believed to be hazardous, but data are lacking on RCRA leach characteristics or other toxicity information. Many of the catalyst materials can be economically recycled for their metal values, particularly when the costs of disposal as hazardous waste are set as the point of reference.

Table 7 summarizes the total estimated costs and energy impact of pollution control for the options presented. The data indicate that air pollution control can add up to 14% of base plant annualized costs, water pollution control up to about 9%, and solid/hazardous waste disposal up to 3.3%, or up to 26% for controls in all media.

Energy requirements for pollution control range from 4.4 to almost 11% of plant input energy, with water pollution control contributing over 60% of the requirement. The differences in energy requirements between the control options are not especially large.

TABLE 7. SUMMARY OF TOTAL COSTS AND ENERGY IMPACTS FOR POLLUTION CONTROL IN AN INTEGRATED FACILITY

Pollution Control Technology	% of Total Annualized Costs		% of Plant Energy Reqmts.	
	Option I	Option II	Option I	Option II
Air	9.1 - 14.1	5.8 - 11.7	1.6 - 2.8	1.4 - 2.5
Water	3.7 - 8.5	3.1 - 7.5	3.0 - 8.0	3.0 - 7.9
Solid Waste	2.6 - 3.3	1.8 - 2.3	0.06 - 0.08	0.04 - 0.06
Total Percent of Base Plant	15.4 - 25.9	10.7 - 21.5	4.7 - 10.9	4.4 - 10.5

INITIAL EFFORT ON A POLLUTION CONTROL GUIDANCE DOCUMENT; DIRECT LIQUEFACTION

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(ABSTRACT)

Development of the pollution control guidance document (PCGD) for direct coal liquefaction is preceding in parallel with the permitting and construction of the first demonstration-size liquefaction plant, the SRC-II unit in Ft. Martin W.V. In addition to the SRC-II process, the PCGD will provide guidance for the other major liquefaction technologies: SRC-I, H-Coal, and Exxon Donor Solvent.

The control technology guidance will be related to baseline designs prepared for each of the four liquefaction processes, sized at 100,000 bbls/day production. The baseline designs are composed of material balance flowsheets and uncontrolled waste stream calcuations, using plant configurations which are most likely to occur in future commercial size plants. Variations of the baseline designs will be considered if they affect control decisions. A range of feed coals have been selected for the baseline cases, with at least one common coal type that could be used by all four processes. The present effort is focused on identification of the pollutants of concern using pilot-plant test data from coal liquefaction developers, DOE, and EPA sponsored testing programs. These data will be evaluated with a variety of engineering analysis methodologies, so that the subsequent examination of control options can be carried out.

The range of control options--air, water, solid waste--will be selected from those methods that have a known track record in related industrial applications, such as petroleum refining, coke ovens, and mining.

The control technologies will be charaterized parametrically according to the inlet stream compositions and quantities, and their percentage release of specific pollutants. Finally, the cost of control will be developed according to the same parameters, with a range of costs obtained depending on the complexity and efficiency of control.

INITIAL EFFORT ON A POLLUTION CONTROL GUIDANCE DOCUMENT; DIRECT LIQUEFACTION

DIRECT COAL LIQUEFACTION PROCESSES

The Direct Liquefaction PCGD will be based on those liquefaction processes that are the closest to commercialization. The SRC-I, SRC-II, H-Coal and Exxon Donor Solvent (EDS) processes are all at an advanced stage of pilot-plant development, and the SRC-I and SRC-II processes will be expanded to demonstration size units in the next few years. Although other "second generation" direct liquefaction processes are in bench-scale development, they will not be ready for commercialization until the early 1900's. The current status of the advanced development processes are:

- The SRC-I process is being tested in a 50 tons/day pilot plant at Fort Lewis, Washington, and in a 6 tons/day process development unit at Wilsonville, Alabama. Preliminary designs for a demonstration plant, to be located near Newman, Kentucky, were completed on July 1979. The demonstration plant is designed to produce the equivalent of 20,000 barrels of oil per day, and is scheduled to be completed by 1984. Current plans call for enlargement of the facility to produce the equivalent of 100,000 barrels of oil per day in 1990.

- The SRC-II process is also being tested in the pilot plant at Fort Lewis, Washington. Preliminary designs for a SRC-II demonstration plant, to be located at Fort Martin, West Virginia, were completed in July 1979. The demonstration plant is designed to process 6,000 tons of coal per day to produce the equivalent of 20,000 barrels of oil per day. Completion of the plant is scheduled for 1984.

- The EDS pilot plant at Baytown, Texas, started up on June 24, 1980. This plant has a capacity of 250 tons per day of coal feed to produce approximately 600 barrels per day of synthetic liquid fuel. A 70 tons per day Flexicoking unit at the same site is planned to be completed in the second quarter of 1982. The design of a demonstration plant could begin as early as the fourth quarter of 1982, leading to a start-up date of about 1988.

- The H-Coal pilot plant at Catlettsburg, Kentucky, has been operational since June 1980. This plant has a capacity of 600 tons per day of coal feed. Support work in a 3 tons per day process development unit is also continuing. Groundbreaking for a commerical plant in Breckinridge, Kentucky, is planned for 1983. The commercial plant is expected to start production as early as 1987.

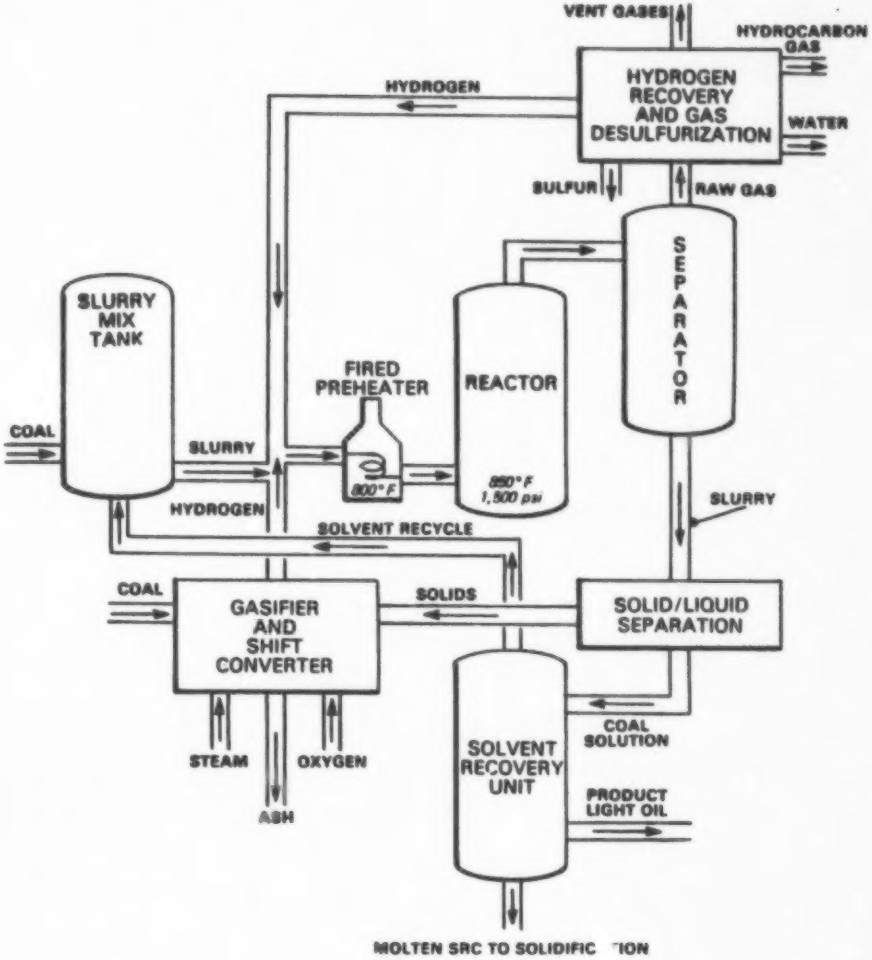
SRC-I PROCESS(1)

The SRC-I is a process for converting high-sulfur, high-ash coals to a low-sulfur and substantially ash-free solid fuel. In the SRC-I process (Figure 1), feed coal is pulverized and slurried in a process-derived solvent. This slurry is then pumped to reaction pressure (2000 psig), mixed with hydrogen-rich recycle gas, and then heated to reaction temperature in a fired-heater. Within the fired-heater, coal dissolution is accomplished and hydrogenation reactions begin. At the exit of the fired-heater, hot hydrogen makeup gas from a hydrogen makeup area is added to the slurry, and the mixture is sent to the dissolver.

The dissolver effluent is flashed. The raw gas is sent to gas purification, and the slurry containing unconverted coal and ash from the low-pressure flash is sent to a vacuum column, where process solvent and lighter components are removed from the SRC slurry. The SRC ash slurry is then sent to solvent deashing unit, where it is separated into SRC and ash concentrates. The ash concentrate, consisting of ash and unreacted coal, and some residual SRC, is gasified with steam and oxygen. The syngas produced, after shift conversion and acid gas removal, is converted to hydrogen and sent to the dissolver unit as makeup. The major portion of the SRC concentrate is solidified into the primary final product, solvent refined coal.

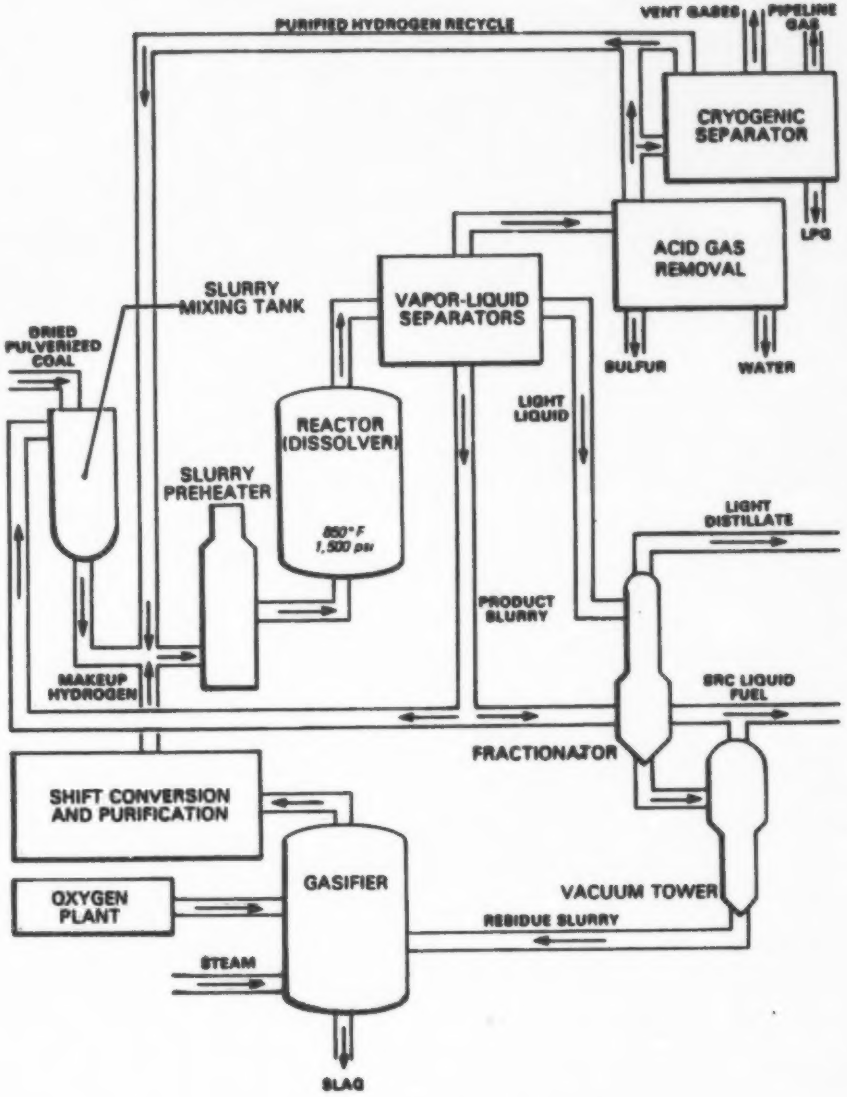
SRC-II PROCESS(2)

The SRC-II process is designed to produce low-sulfur liquid fuel from high-sulfur bituminous coals. As shown in Figure 2, raw coal is pulverized, mixed with a recycle slurry stream from the process, and then pumped together with recycle and makeup hydrogen through a preheater to a dissolver operated at high temperature and pressure. The coal is first dissolved in the liquid portion of the recycle slurry and then largely hydrocracked to liquids and gases. Much of the sulfur, oxygen, and nitrogen in the original coal is hydrogenated to hydrogen sulfide, water, and ammonia, respectively. The rates of these reactions are increased by the catalytic activity of the undissolved mineral residues. The recycle of a portion of the product slurry contributes substantially to the process by increasing the concentration of catalytic mineral residue in the reactor.


VENT GASES
HYDROCARBON GAS
HYDROGEN
HYDROGEN RECOVERY AND GAS DESULFURIZATION
WATER
SULFUR
RAW GAS
SEPARATOR
SLURRY MIX TANK
FIRED PREHEATER
REACTOR
COAL
SLURRY
800° F
850° F 1,500 psi
HYDROGEN
SLURRY
SOLVENT RECYCLE
COAL
SOLIDS
GASIFIER AND SHIFT CONVERTER
SOLID/LIQUID SEPARATION
COAL SOLUTION
SOLVENT RECOVERY UNIT
STEAM
OXYGEN
ASH
PRODUCT LIGHT OIL
MOLTEN SRC TO SOLIDIFIC TION

SRC-I PROCESS

Figure 1.


PURIFIED HYDROGEN RECYCLE
VENT GASES
PIPELINE GAS
CRYOGENIC SEPARATOR
LPG
ACID GAS REMOVAL
SULFUR
WATER
SLURRY MIXING TANK
DRIED PULVERIZED COAL
VAPOR-LIQUID SEPARATORS
REACTOR (DISSOLVER)
850° F
1,500 psi
SLURRY PREHEATER
LIGHT LIQUID
LIGHT DISTILLATE
PRODUCT SLURRY
MAKEUP HYDROGEN
SRC LIQUID FUEL
FRACTIONATOR
SHIFT CONVERSION AND PURIFICATION
GASIFIER
OXYGEN PLANT
VACUUM TOWER
RESIDUE SLURRY
STEAM
SLAG

SRC-II PROCESS
Figure 2.

The dissolver effluent is separated into gas, light hydrocarbon liquid and slurry streams using conventional flashing and fractionation techniques. A portion of the mineral residue slurry and hydrocarbon liquid from the separation area is recycled to blend with the feed coal in the slurry preparation plant. The balance of the mineral residue slurry is vacuum flashed to recover the fuel oil product.

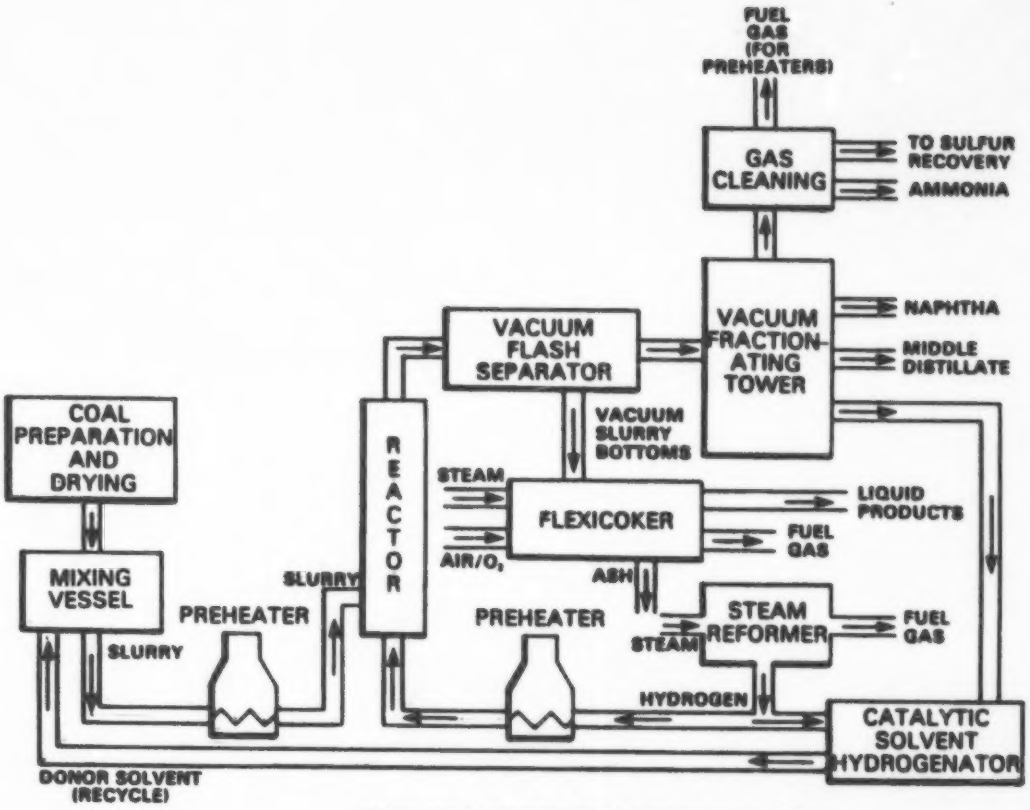
The dissolver area gas stream (consisting primarily of hydrogen, light hydrocarbons, and hydrogen sulfide) is treated for liquid hydrocarbons and acid gas removal, and the major portion of this gas is then recycled to the process. Makeup hydrogen for the process is produced by the gasification of mineral residue slurry to produce synthesis gas, followed by shift conversion.

Liquid products from the main process area are refined in the fractionation section into naphtha, light fuel oil, and heavy fuel oil. Various by-product liquid and gas streams are treated further in the gas plant to produce propane, butane, and pipeline gas. Secondary recovery plants are provided to recover ammonia, tar acids and sulfur.

EDS PROCESS (3)

The Exxon Donor Solvent (EDS) is a noncatalytic process that liquefies coal by the use of a hydrogen donor solvent obtained from coal-derived distillate. The donor solvent transfers hydrogen to the coal, thus promoting the liquefaction of coal.

In the EDS process (Figure 3), ground coal is slurried with the recycle donor solvent. The slurry is heated by a fired-heater, and preheated hydrogen is added. The liquefaction reaction is carried out in a tubular reactor at 800°-900° F and 2000 psig. Products from the liquefaction reactor are sent to several stages of separation units for recovery of gas, naphtha, middle distillate, and bottoms comprised primarily of unreacted coal and mineral matter. Solid and liquid products are separated by distillation.


FUEL GAS (FOR PREHEATERS)
GAS CLEANING
TO SULFUR RECOVERY
AMMONIA
VACUUM FRACTION-ATING TOWER
NAPHTHA
MIDDLE DISTILLATE
VACUUM FLASH SEPARATOR
VACUUM SLURRY BOTTOMS
COAL PREPARATION AND DRYING
MIXING VESSEL
SLURRY
PREHEATER
SLURRY
REACTOR
STEAM
AIR/O₂
FLEXICOKER
LIQUID PRODUCTS
FUEL GAS
ASH
STEAM
STEAM REFORMER
FUEL GAS
PREHEATER
HYDROGEN
CATALYTIC SOLVENT HYDROGENATOR
DONOR SOLVENT (RECYCLE)

EXXON DONOR SOLVENT PROCESS

Figure 3.

The heavy vacuum bottoms from distillation are fed to a FLEXICOKING unit with air and steam to produce additional distillate liquid products and a low Btu fuel gas for process furnaces. In the FLEXICOKING unit, essentially all organic material in the vacuum bottoms is recovered as liquid product or combustible gases.

Hydrogen for in-plant use is produced by steam reforming of light hydrocarbon gases. An alternative method for hydrogen production is partial oxidation of the heavy vacuum bottoms or of coal.

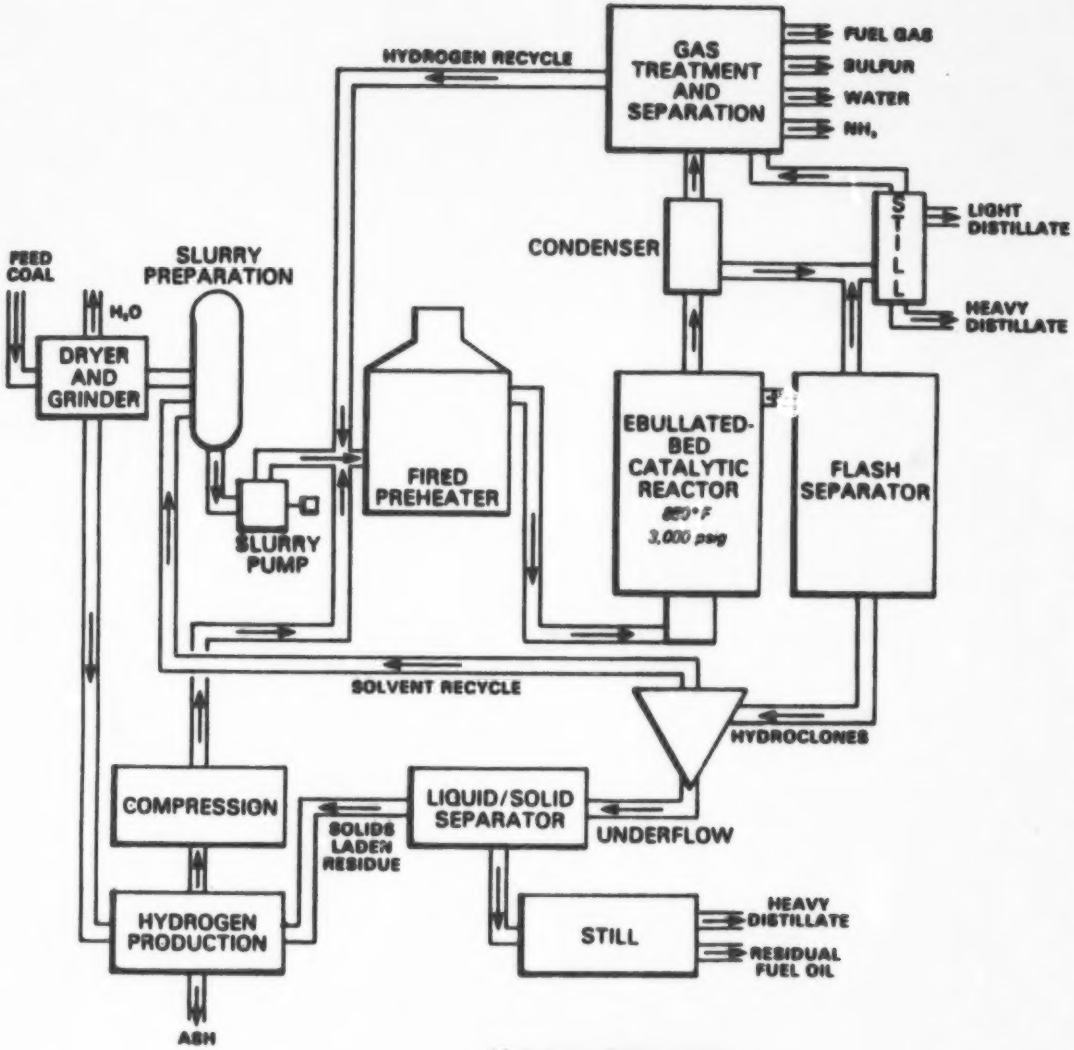
H-COAL PROCESS(4)

The H-Coal process is a catalytic hydroliquefaction process that converts high-sulfur coal to either a low-sulfur boiler fuel or to a refinery syncrude. In this process (Figure 4), coal is dried and crushed, then slurried with recycled oil and pumped to a pressure of 2000 atm. Compressed hydrogen is added to the slurry, and the mixture is preheated and charged continuously to the bottom of the ebullated-bed catalytic reactor. Upward passage of the internally recycled reaction mixture maintains the catalyst in a fluidized state (catalyst activity is maintained by the semicontinuous addition of fresh catalyst and the withdrawal of spent catalyst). Typical mixing temperature entering the reactor is 600° to 700° F.

The vapor product leaving the top of the reactor is cooled to condense the heavier components as a liquid. Light hydrocarbons, ammonia and hydrogen sulfide, are absorbed and separated from the remaining gas, leaving a hydrogen-rich gas which is recompressed and recycled to be combined with the input slurry. The liquid-solid product, containing unconverted coal, ash, and oil, is fed into a flash separator. The bottoms product containing solids and heavy oil is further separated with a hydroclone, a steam stripper, and a vacuum still.

The gas and liquid products (hydrocarbon gas, hydrogen sulfide, ammonia, light and heavy distillates, and residual fuel) may be further refined while heavy distillate is recycled as the slurry medium.

Fig 4


FEED COAL
H_2O
DRYER AND GRINDER
SLURRY PREPARATION
SLURRY PUMP
HYDROGEN RECYCLE
FIRED PREHEATER
GAS TREATMENT AND SEPARATION
FUEL GAS
SULFUR
WATER
NH_3
CONDENSER
STILL
LIGHT DISTILLATE
HEAVY DISTILLATE
EBULLATED-BED CATALYTIC REACTOR
850°F
3,000 psig
FLASH SEPARATOR
SOLVENT RECYCLE
HYDROCLONES
UNDERFLOW
LIQUID/SOLID SEPARATOR
SOLIDS LADEN RESIDUE
STILL
HEAVY DISTILLATE
RESIDUAL FUEL OIL
COMPRESSION
HYDROGEN PRODUCTION
ASH

H-COAL PROCESS

Figure 4.

APPROACH TO PROCESS CHARACTERIZATION

A methodology has been established that uses a baseline design for each process, sized at 100,000 bbls/day net equivalent of product liquids, fuel gases, and coal-replacement solid products. The design and pilot-plant experience of the several liquefaction processes has been limited to certain types of feed coals, so that the guidance document will have to recognize that expected variations in proposed liquefaction plant feed coals will be limited to an experience range. This will be particularly critical for the non-catalytic SRC-I and SRC-II processes, which depend on the catalytic properties of constituents found in bituminous coals for adequate yields. At least two feed coals will be used in the PCGD analysis for each given liquefaction process, with Illinois No. 6 grade being common to all processes. Initial baseline design concepts are being prepared and submitted for comment to the developers of the four liquefaction processes. In most cases, commercial design concepts of these process developers are somewhat of a moving target, and it is generally recognized that the baseline design cases will not necessarily represent a particular final design configuration. The process developers will be asked to confirm that proposed baseline designs represent a feasible plant configuration, and to estimate the impact that various design options may have on the waste stream characteristics of a baseline case. The goal of this preparatory step is to provide a process description that EPA permit reviewers can reasonably compare with submitted applications.

The initial baseline designs, including material balances and flowcharts which identify the major and minor stream constituents at key points, are being prepared by incorporating pilot plant test results and engineering estimates with commerical-plant design cases that have been released by each process developer. A critical feature of these analyses will be the validation and interpretation of pilot-plant test data. Determinations will be made as to whether these data were obtained under steady-state conditions, using standardized sampling and analysis techniques. The uncontrolled constituents in each waste stream (gaseous, liquid, or solid) have to be estimated in these baseline design cases in order to realistically evaluate control technology requirements. A substantially inaccurate estimate could lead to either inadequate control technology specifications or unnecessary pollution control investment requirements.

The major gaseous emission streams requiring control include the following:

- Fugitive dust emissions from coal storage
- Fugitive dust emissions from coal and slag handling
- Fugitive hydrocarbon emissions from valves, flanges, and seals
- Fugitive hydrocarbon emissions from product and byproduct storage
- Off gas from coal dryer
- Acid gases containing H_2S, CO_2,COS, CS_2, and mercaptans and NH_3 from sour water stripping units
- Flue gas from process heaters
- Flue gas from steam plant
- Flue gas from power plant
- Evaporation and drifts from cooling towers

An essential element of these uncontrolled stream charaterizations is the fugitive vapor emission category. A very limited amount of ambient organic vapor sampling has been conducted at the SRC-II pilot plant at Ft. Lewis. Although this sampling and analysis effort cannot be directly extrapolated to full-scale plants because of operations which are unique to the pilot plant, the measurements offer some insight into the ability of heavy organics (e.g., POM) to disperse into the surrounding atmosphere as a result of small vapor emissions.

The major wastewater streams requiring control include the following:

- Sour process wastewater from vapor washes, condensers, fractionator overhead drums, sulfur recovery plant, and coal slurry mixing operation
- Cooling tower blowdown
- Boiler blowdown
- Coal pile runoff
- Oily water runoff from processing areas
- Miscellaneous small wastewater streams

Untreated wastewater characterizations will be derived from measurements conducted by process developers, EPA, and DOE sampling and analysis efforts. Some judgements will have to be made concerning the effects of coal feed characteristics and process operating configurations on these measurement values. Most of these measurements have focused on process wastewater (or "sour water", following refinery terminology). Other anticipated sources of wastewater include coal pile and area runoff, cooling tower blowdown, and discharge from dust collection and conveying use. These other catagories are analagous to related discharges from coal handling and other industrial operations.

Solid waste discharges will include gasifier slag (from hydrogen synthesis), spent catalysts, wastewater and raw water treatment sludges, and possibly non-salable byproduct residues. Some limited amount of leaching tests have been done to characterize gasifier slags and some residue material, but more work will have to be done before a determination can be made as to the possible characterization of these wastes as non-hazardous or hazardous.

CONTROL TECHNOLOGY EVALUATION

EPA permit reviewers will be faced with a range of possible control technologies connected with direct liquefaction process designs. To help the permit reviewers in their examination of submitted plans, a number of best-available-control-technology (BACT) options will be evaluated for each potential waste stream for each of the four major liquefaction processes. In addition, two levels of control effectiveness will be included. The evaluation of each control technology will include the efficiency of pollutant removal from a stream, multipollutant removal capability, installed and operating cost, reliability, turndown ratio, sensitivity to process stream conditions, energy consumption, and any other operating history information such as maintenance requirements.

A primary air pollution control concern in liquefaction processes is the treatment of acid gases generated in the liquefaction reactor, from sour water stripping, and in gasification of residiuum streams to make hydrogen. A typical process design method for removing CO_2 and H_2S constituents from these streams is some form of absorption, such as DEA, Selexol, or Benfield processes. The H_2S-rich gas stream stripped from the absorbing liquid constitutes the acid gas stream requiring further control. Representative acid gas stream compositions are shown in Table 1. These streams can be subjected to two stages of sulfur removal. Concentrated (20-70%) H_2S streams will be handled by a process technology that does bulk sulfur removal. The Claus sulfur recovery process is the most likely candidate for this job, based on a long history of refinery and gas processing experience, but investigations are underway to evaluate Stretford process applicability with high H_2S concentrations. Residual sulfur removal options are numerous; some technologies accept Claus tail-gas directly and hydrolize SO_2 to H_2S, others require oxidation of H_2S in the stream to SO_2. The PCGD evaluation will evaluate many combinations of control technology types to establish BACT performance and cost ranges.

An example of a number of combinations is shown in Table 2, using two bulk-sulfur removal options, three residual sulfur removal options, and a final incineration step option (for potential trace organic removal and oxidation of trace sulfur to SO_2).

TABLE 1. REPRESENTATIVE ACID GAS STREAMS FROM DIRECT LIQUEFACTION

Constituent concentration (mol%)	SOURCE		
	Stripper offgas from process gas treating	Stripper offgas from syngas purification	Sour water stripper offgas
H_2S	75	30	25
CO_2	20	50	50
CO	Trace	10	-
COS	Not determined	.0003	-

TABLE 2

Options / Combinations	Bulk-S Removal		Residual-S Removal			Incineration
	Claus	Stretford	Beavon	SCOT/ SUPERSCOT	Wellman-Lord	
1		●	●			●
2		●		●		●
3		●			●	
4	●		●			●
5	●			●		●
6	●				●	

An additional combination will be examined for streams containing very low H_2S (or COS, CS_2 etc.) concentrations, since these may be directly incinerated.

Both capital and operating costs will be determined according to the standardized guidelines prepared by IERL/RTP(5). The impacts on other media for any of the pollution control technologies will also be quantified; the acid gas gas treatment systems above will produce spent catalysts as well as minor liquid purge streams. A substantial non-hazardous solid waste quantity will require disposal planning if the recovered sulfur is not salable. Wastewater treatment guidance is expected to emphasize the stripping of ammonia and H_2S from sour water streams, and the absorption of phenols. The sequence of these byproduct recovery steps may be significant to recovery efficiency.

Subsequent treatment steps will be selected to minimize the release of trace organics and heavy metals to the environment. Investigations of "zero discharge" evaporative methods are currently being compared with more conventional biological treatment technologies. A high degree of water reuse will be emphasized no matter what treatment method is used.

The impact on solid waste handling and management requirements may be substantial, depending on the control options recommended for wastewater treatment and air pollution control technology. The cost and stringency of solid waste management practices will be greatest for wastes designated as hazardous under RCRA definitions.

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APPENDIX: ATTENDEES

ATTENDEES

FUEL CONVERSION TECHNOLOGY, V SYMPOSIUM
September 16-19, 1980
Chase-Park Plaza Hotel
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Thoem	Terry L.	Suite 900, 1860 Lincoln St.	Denver	CO	80295	U.S. EPA, Region VIII
Thomas	Susan J.	4 Research Place	Rockville	MD	20850	NUS Corporation
Thomas	William C.	8500 Shoal Creek Boulevard	Austin	TX	78758	Radian Corporation
Trabert	Angela L.	816-16th Street	Wilmette	IL	60091	
Tranquill	Paul C.	Midland Building	Cleveland	OH	44115	The Standard Oil Co.
Tyndall	Frank	500 Eastowne Drive	Chapel Hill	NC	27514	GCA Corporation
Vlahakis	John	12th and Pennsylvania Ave., N. W.	Washington	DC	20461	Department of Energy
Vyas	Kaushik	P. O. Box 880	Morgantown	WV	26505	EG&G
Wadden	Richard	P. O. Box 6998, School/Public Health	Chicago	IL	60680	University of Illinois
Wallace	Anna W.	P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
Wammel	A. W.	P. O. Box 509	Beacon	NY	12508	Texaco Inc.
Weinreich	Gary N.	One Woodward Avenue	Detroit	MI	48226	American Natural Service Co.
Weitzel	Richard L.	509 Estes Avenue	Schaumburg	IL	60193	Ecological Analysts, Inc.
West	Chris	MD-51	Research Triangle Park	NC	27711	U.S. EPA
Wiener	Richard	One Penn Plaza	New York	NY	10001	Envirotech/Chemico
Williamson	Phebus C.	Ammonia from Coal Projects	Muscle Shoals	AL	35660	Tennessee Valley Authority
Willson	Warrack G.	P. O. Box 8213, University Station	Grand Forks	ND	58202	Grand Forks Energy Technology Center
Wipperman	Robert C.	100 Federal S.	Boston	MA	02110	Herrick & Smith
Witmer	Fred E.	Mailstop E-201, Env. Safety & Eng.	Washington	DC	20545	Department of Energy
Yen	Alan F.	P. O. Box 2752	Allentown	PA	18001	International Coal Refining Company
Yu	Kar Y.	One Space Park Drive, R4/1136	Redondo Beach	CA	90278	TRW, Inc.
Yu	Wen C.	7929 Westpark Drive	McLean	VA	22102	UOP/SDC
Zaklan	Gerri	1313 Dolley Madison Boulevard	McLean	VA	22101	Dynalectron
Zoueshtiagh	Nahid	50 Beale Street	San Francisco	CA	94119	Bechtel